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THE PHOTOLYSIS AND THERMOLYSIS
OF IODOBENZENE DICHLORIDE

BY



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A THESIS

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ABSTRACT

An investigation of the photolysis and thermolysis of iodobenzene dichloride (IBD) was carried out in carbon tetrachloride. The major products from photoinitiated decompositions at 0° are listed below as mole/mole IBD yields: hydrogen chloride (40%), iodobenzene (7-17%), 2-chloriodobenzene (II) (13-17%), and 4-chloriodobenzene (III) (10-25%). Small amounts of chlorobenzene (3%), 1,2-dichlorobenzene, 1,4-dichlorobenzene, ring dichlorinated benzene, molecular chlorine and traces of 3-chloriodobenzene were also detected. Essentially the same product distributions were observed in non-irradiated decompositions at 40°, except that the amount of III increased so that the mole ratio of II/III was reduced from 1.7 to 0.7. Traces of dichlorobenzenes were observed, but no 3-chloriodobenzene was detected in the products from thermally induced decompositions.

Neither the reaction times required for rearrangement of IBD nor the products observed from the rearrangements were affected by trace amounts of several common free-radical inhibitors.

Decompositions of IBD in solvent containing toluene resulted in formation of benzyl chloride (IV)

and ring-chlorinated toluene (V) as major products. The ratio of IV/V varied from 1.37 (0° , $h\nu$) to 0.37 (40° , dark) in reactions that were carried out in irradiated and non-irradiated conditions.

Anomalously large yields of chlorobenzene were observed in the products from decomposition of IBD that were carried out in solvent containing benzene.

Although reactions of IBD with toluene or benzene superceded the rearrangement of IBD itself, measurable yields of rearrangement products were detected.

On the basis of the results from reactions with the aromatic substrates and from the inhibition experiments rearrangement of IBD occurs by concurrent ionic and free-radical reaction schemes. The free-radical mechanism, characterized by large ratios of II/III, predominates in the photoinitiated decompositions. The ionic mechanism, characterized by small ratios of II/III, predominates in the thermally induced reactions.

Geminant cage recombination of atomic chlorine and phenylchloroiodinyl radicals ($\text{PhICl}^\bullet$) appears to be the homolytic reaction sequence involved in the rearrangement of IBD. Recombination of chloronium ions with phenylchloroiodinyl anions (PhICl^-) and recombination of chloride ions with phenyl chloroiodinyl cations (PhICl^+) are proposed as equally feasible, but indistinguishable ionic reaction sequences for rearrangement of IBD.

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INTRODUCTION

The mechanisms of thermally induced and photoinitiated chlorination reactions in which iodobenzene dichloride (IBD) is used as a chlorinating reagent have been under investigation since 1937 (1, 2, 10-18 inclusive). It has been established that, in the absence of ionic catalysts, addition to double bonds (1) and substitution reactions of alkanes (2) proceed by free-radical mechanisms when IBD is used as a chlorinating agent in non-polar solvents. However, if these halogenation processes are inhibited, rearranged IBD becomes predominant in the reaction products at the expense of chlorinated substrate. The thermal (3) and photoinitiated (4) rearrangements of solid IBD have been examined only superficially; hence a more detailed study of the rearrangement constitutes the topic for the present investigation.

Historical Review

Iodobenzene dichloride, the first organic compound reported to contain poly-valent iodine, was prepared initially by Willgerodt in 1885. Chlorine and iodobenzene were liberated when the yellow solid decomposed either on standing in moist air or upon heating (3).

Keppler observed that decomposition of solid IBD in sealed reaction vessels was light catalysed. Chlorine and hydrogen chloride were detected as gaseous products and

4-chloriodobenzene was isolated from the reaction mixture by recrystallization from alcohol (4). Equation 1 was proposed for the decomposition of IBD.



McCombie and his associates investigated the thermally induced decompositions of 4-hydroxyiodobenzene dichloride (5), 2-hydroxyiodobenzene dichloride (6), and of several 4-alkoxyiodobenzene dichlorides (7). The parent iodo compound bearing a chlorine substituted para (if that position was not already occupied) or ortho to the oxygen containing substituent was isolated from the final reaction mixtures of all decompositions that were carried out.

Ingold et al. observed that decomposition of 2-methoxyiodobenzene dichloride resulted in formation of 3-chloro-6-methoxyiodobenzene (8). These results complied with the observations of McCombie. Ingold also demonstrated that an intermolecular reaction scheme was possible for rearrangements of aryl-iodo dichlorides by carrying out a reaction between acetanilide and 3-chloro-6-methoxyiodobenzene dichloride in heated chloroform (8). 4-Chloroacetanilide and 3-chloro-6-methoxyiodobenzene were the only products isolated from the reaction mixture.

At this point, the thermally induced reactions of substituted aryl-iodo dichlorides were established as intermolecular processes. Garvey, Halley and Allen

pioneered the use of IBD as a chlorinating agent for the addition of chlorine to unsaturated compounds (9). Products from additive chlorination of several olefins, prepared by refluxing IBD and olefin in ethylene dichloride, were identical to those observed when molecular chlorine was used as the halogenating agent; but the former reactions proceeded under milder conditions. Notable exceptions were benzene and cinnamic acid which failed to react when treated with IBD.

Bloomfield quantitatively added chlorine to natural rubber (<4% substitution) by refluxing the rubber with IBD in carbon tetrachloride (10). Addition of p-hydroquinone (a free-radical inhibitor) to the reaction mixture resulted in an inhibition of the addition reaction and was accompanied by a 23% increase in a substitution reaction. A thermally induced free radical-chain, with chain propagation by atomic chlorine, was proposed as the mechanism of the addition reaction. Bloomfield's results were reproduced and his mechanism subsequently was confirmed by other workers (11).

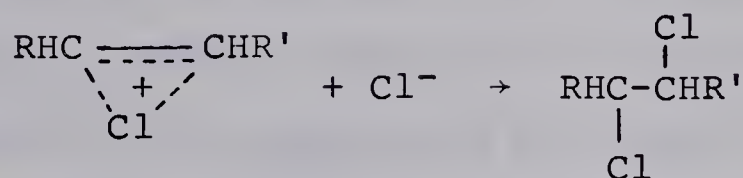
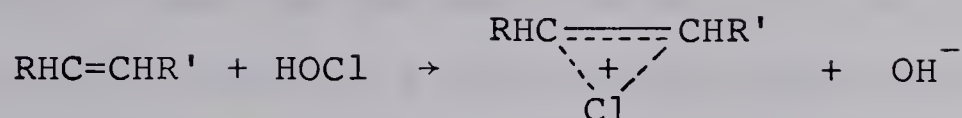
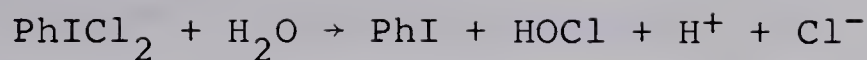
Berg and Wallis prepared two of four possible dichlorinated isomers of cholesteryl benzoate in 80% yields by reacting cholesteryl benzoate and IBD in refluxing carbon tetrachloride (12). Alternatively, chlorination of cholesteryl benzoate with molecular chlorine resulted in formation of only one dichloride isomer along with numerous

unidentified side products.

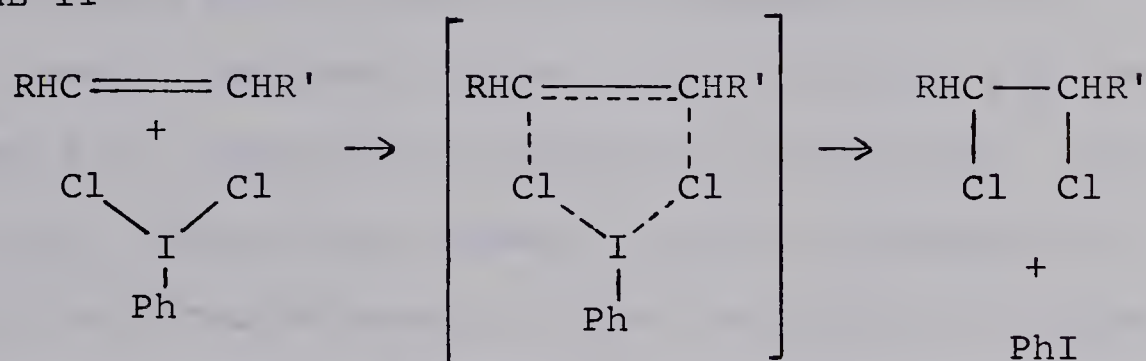
Barton and Miller examined the stereochemistry of chlorine addition to the cholesteryl system (13). Only trans-5 α ,6 β -dichlorocholestan-3 β -yl benzoate was isolated when molecular chlorine was used as the chlorinating agent. Addition of chlorine to cholesteryl benzoate was effected by refluxing the benzoate with IBD in anhydrous carbon tetrachloride. The addition resulted in formation of the same products reported by Berg and Wallis; namely, cis-5 α ,6 α - and trans-5 α ,6 β -dichlorocholestan-3 β -yl benzoate in a ratio of 5.5:1. Barton also observed that an increase in the proportion of the trans isomer accompanied addition of water to the solvent (carbon tetrachloride) for chlorinations of the cholesteryl system when IBD was used as the chlorinating agent. The ratio of the cis to the trans isomers was reduced to 0.14:1 in the reactions that were carried out in media having a 1:1 mole ratio of cholesteryl benzoate to water. Consequently, Barton proposed a trans ionic addition in the presence of water (Scheme I) and a cis molecular addition in anhydrous solvents (Scheme II) as possible mechanisms for the addition of chlorine to double bonds when IBD was employed as a chlorinating reagent.

Cristol et al. isolated a 28% yield of trans-1,2-dichloroacenaphthene from a reaction of

SCHEME I



SCHEME II



acenaphthylene with IBD in anhydrous chloroform which contained trace amounts of sym-trinitrobenzene (a free-radical inhibitor) (14). Only a 10% yield of the trans dichloride was obtained from reactions carried out under otherwise identical reaction conditions without added inhibitor. Furthermore, cis-1,2-dichloroacenaphthene was formed exclusively in chlorinations of acenaphthylene when molecular chlorine was used as a chlorinating agent in anhydrous chloroform. These results contrasted with the observations of Berg and Wallis, and those of Barton and Miller.

Summerbell and Lunk presented other contradictory evidence regarding the addition of chlorine to olefins when IBD was used as a chlorinating agent (15).

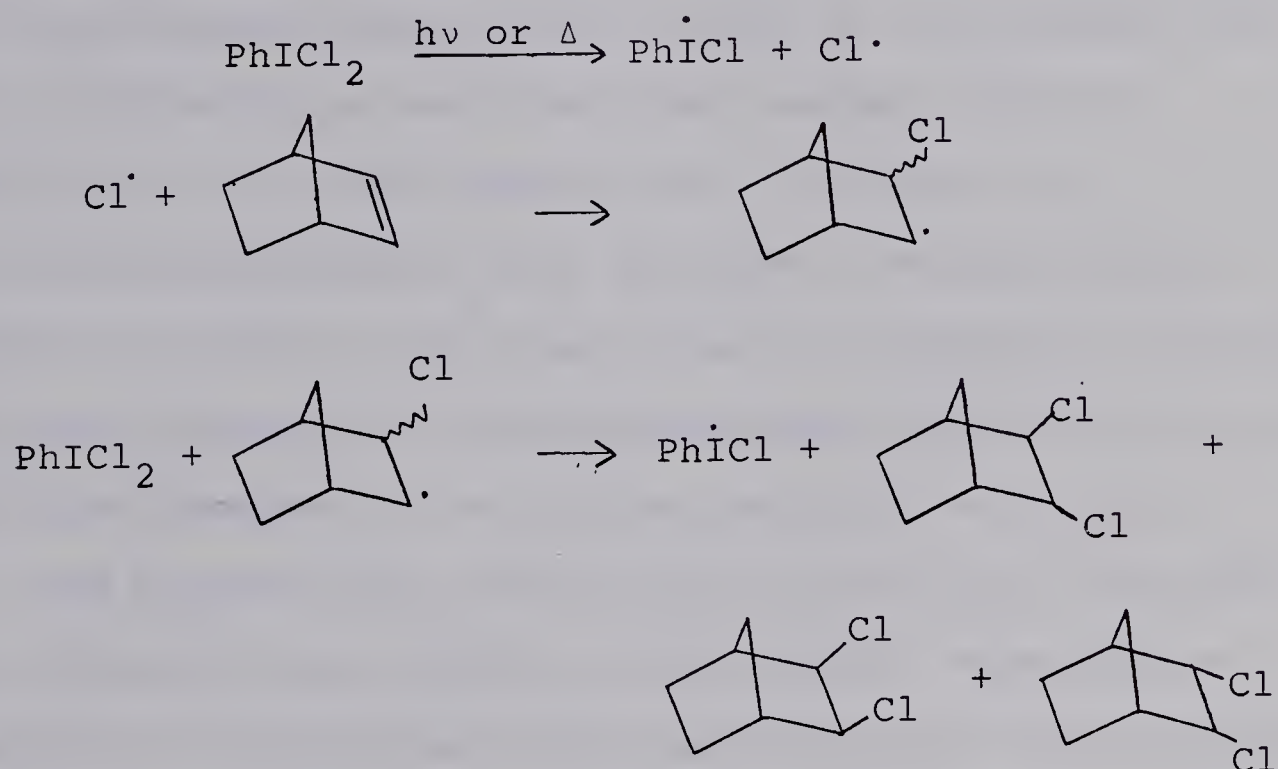
Chlorinations of p-dioxene with molecular chlorine in anhydrous carbon tetrachloride resulted in formation of a mixture of 61% trans- and 41% cis-2,3-dichlorodioxane. Conversely, a mixture of 95% trans and 5% cis dichloride was obtained from a reaction of p-dioxene with IBD.

Poutsma employed both molecular chlorine and IBD as reagents for addition of chlorine to norbornene (16). Molecular chlorine was added, at 25° in darkness, to solutions of norbornene in carbon tetrachloride containing atmospheric amounts of oxygen. Nortricyclylchloride (65%) and exo-2-syn-7-dichloronorbornane, both of which possess skeletally rearranged norbornyl systems, were isolated as major components of the reaction products. Unrearranged trans-2,3-dichloronorbornane (6%) and exo-cis-2,3-dichloronorbornane (4%) were detected as minor products. A mixture of trans-2,3-dichloronorbornane (60%) and exo-cis-2,3-dichloronorbornane (40%) were isolated as the exclusive products from reactions in which IBD and norbornene were refluxed in anhydrous carbon tetrachloride.

Recent investigations by Tanner and Gidley have demonstrated, quite conclusively, that the mechanism for chlorinations of norbornene involves a thermally or

photolytically induced free-radical chain (Scheme III) in which chlorine atoms are the chain carrying species when IBD is used as a chlorinating agent in anhydrous, non-polar solvents (1).

SCHEME III



Atmospheric amounts of oxygen profoundly altered the products obtained from reactions between IBD and norbornene. Total yields of chlorinated norbornane were low in oxygen inhibited reactions, and 50% yields of products from the rearrangement of IBD were detected. The chlorinated norbornanes observed in oxygen inhibited reactions at low temperatures were composed almost entirely of products anticipated from ionic chlorination of norbornene; namely,

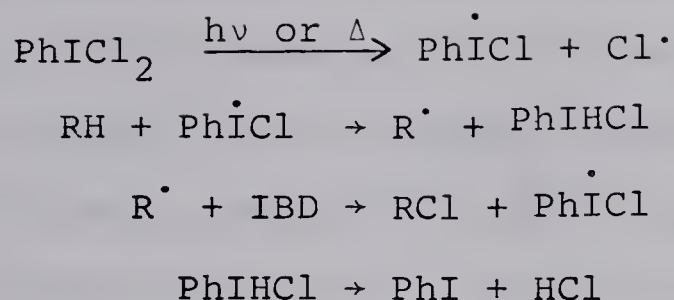
nortricyclyl chloride (79%) and exo-2-syn-7-dichloronorbornane (12%) were obtained. Small amounts (~9%) of unrearranged 2,3-dichloronorbornane, the expected products from free-radical chlorination of norbornene, were also detected in the products. Larger amounts (25-50%) of unrearranged 2,3-dichloronorbornanes were detected in the products from both irradiated and non-irradiated, oxygen inhibited reactions at elevated temperatures. Although the 2,3-dichloronorbornanes were detected in widely varying amounts relative to the total amounts of products, the ratio of trans-/cis-exo-2,3-dichloronorbornane remained consistent with that observed in uninhibited addition reactions.

The mechanism for chlorination of saturated compounds has attracted some attention since Russell observed two anomalies in the products from photoinitiated chlorinations of 2,3-dimethylbutane by molecular chlorine in iodobenzene (17). Firstly, lower than normal yields of chlorinated substrate were observed due to a competing reaction between chlorine and iodobenzene which resulted in formation of IBD. And secondly, a tertiary/primary selectivity of 31:1 was observed for hydrogen abstraction from 2,3-dimethylbutane. A tertiary/primary selectivity of 3.5:1 is observed normally for hydrogen abstraction when molecular chlorine is used as a reagent for photoinitiated halogenation reactions in carbon tetrachloride.

The tertiary/primary selectivity observed for the reactions in iodobenzene exceeded, by far, that anticipated for a solvent effect. The equilibrium which exists between molecular chlorine, iodobenzene, and IBD, heavily favors formation of the dichloride. Since large quantities of IBD were present in the reaction mixtures, Russell proposed that the phenylchloriodinyl radical ($\text{Ph}\dot{\text{I}}\text{Cl}$) was the predominant hydrogen abstracting species. He further proposed that the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical was an exclusive tertiary hydrogen abstracting species. Hydrogen abstraction by the small quantities of atomic chlorine in the reaction mixture was offered as an explanation for the observed primary halogenated products.

Huyser et al., reported 85% yields of cyclohexyl chloride and benzyl chloride when IBD was used as a reagent for photoinitiated halogenation of cyclohexane and toluene at 15° (18). Iodobenzene dichloride was employed as a reagent for photoinitiated halogenation of neat 2,3-dimethylbutane in order to verify existence of the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical as a hydrogen abstracting species. Since only tertiary hydrogen abstraction was observed, the following mechanism (Scheme IV) was proposed for the substitution reactions. The mechanism depicted in Scheme IV involves hydrogen abstraction exclusively by the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical.

SCHEME IV



Tanner and Van Bostelen used IBD as a reagent for photoinitiated chlorinations of 1-chlorobutane, 1-chloropropane, and n-butyronitrile in carbon tetrachloride at 40° (2). The distribution of isomeric products obtained in that manner was similar to that obtained when molecular chlorine was employed as a halogenating reagent for the same compounds. Comparison of the primary:secondary:tertiary selectivities for hydrogen abstraction from n-butane and 2,3-dimethylbutane when IBD was used as the chlorinating agent (1:21:368) with those observed when molecular chlorine was used as the halogenating reagent (1:3.9:5.1) indicated that the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical was a more selective hydrogen abstracting species than atomic chlorine. Selectivities for tertiary/secondary hydrogen abstraction were obtained by carrying out competitive halogenations of norbornane and cyclohexane. The selectivities observed in these experiments were compatible with those above for the respective halogenating agents. Comparison of the deuterium isotope effect observed for halogenations of cyclohexane and

perdeuterocyclohexane when IBD was used as a chlorinating agent (1.9) with that observed when molecular chlorine was used as a reagent (1.4) offered further evidence of the high selectivity possessed by $\text{Ph}\dot{\text{I}}\text{Cl}$ radicals.

The relative reactivities towards halogenation when IBD was used as the halogenating agent were examined within a group of negatively substituted alkanes (1-chloropropane, n-butylronitrile, and 1,1-dichlorobutane) and within a group of unsubstituted alkanes (cyclohexane, 2,3-dimethylbutane, cyclopentane, and norbornane). The relative reactivities observed for chlorinations when IBD was used as the halogenating agent were substantially different from those observed when molecular chlorine was employed as the halogenating agent. The large differences observed in the relative reactivities to chlorination by molecular chlorine and by IBD demonstrated that the hydrogen abstracting species were different for the two reagents. The detailed examination carried out by Tanner and Van Bostelen confirmed that the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical is indeed very selective for hydrogen abstraction from aliphatic hydrocarbons; but high selectivity combined with deactivation by polar substituents may have caused its simulation of the reactivity of atomic chlorine in hydrogen abstraction reactions on the negatively substituted alkanes.

Almost quantitative yields of chlorinated substrate were observed when photoinitiated reactions of IBD were carried out with unsubstituted hydrocarbons in carbon tetrachloride at 40°. In the reactions of IBD with the relatively unreactive, negatively substituted hydrocarbons only 50% yields of chlorinated products were obtained while 35% yields of products from the rearrangement of IBD were observed. The recurring observation of IBD rearrangement products, once again when facile processes with substrates were deterred, motivated us to carry out a thorough investigation of the IBD rearrangement.

Structure and Bonding of IBD

X-Ray structural determinations of solid IBD were carried out by Archer and van Schalkwyk (19). Examination of IBD dissociation in various solvents was carried out by Keefer and Andrews (23, 24) as well as by Zappi and Cortelezzi (21). Assessment of the results obtained from the dissociation and X-ray investigation mentioned above has provided some insight into the structure and bonding of IBD.

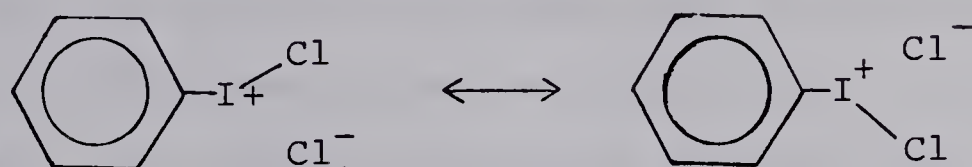
Archer and van Schalkwyk have completed an X-ray structural determination of solid IBD and have found that the molecule is T-shaped, containing a linear, symmetrical chlorine-iodine-chlorine group almost perpendicular

($86 \pm 1^\circ$) to the plane of the benzene ring (19). The molecule is believed to exist in a trigonal-bipyramidal structure having the ring and two lone pairs of electrons situated at the equatorial positions, and with two chlorine atoms occupying the apices. The I-Cl bond length of $2.54 \text{ \AA}$ is larger than the sum of the normal covalent radii ($2.32 \text{ \AA}$) of chlorine and iodine atoms which, at least partially, explains the observation that energy required for either homolytic or heterolytic bond cleavage is less than that required (57.5 kcal/mole) for rupture of normal chlorine-iodine bonds (20).

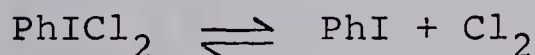
Concluding from results of molecular weight determinations and electrical conductivity measurements of IBD in various solvents, Zappi and Cortelezzi proposed that dissolved IBD can dissociate into iodobenzene and molecular chlorine entirely by a molecular process (21).

LeFevre and LeFevre have observed that, in benzene solution, the dipole moment of IBD is 1.3D larger than that of iodobenzene (22). Evidence is presented indicating that the moment of an I-Cl bond may be between 0.9 and 1.5 Debye units. Assuming that the I-Cl bonds in IBD possess moments equal to 1.3 Debye units. LeFevre and LeFevre hypothesized that, in benzene solution, the -ICl_2 unit in IBD exists as a trigonal planar entity, in which the Cl-I-Cl bond angle is necessarily 120° . They also

proposed that if the trigonal planar conformation existed, a resonance stabilized bond between the chlorine and iodine atoms was possible.



Other evidence supporting the notion of a hybridized Cl-I bond and for involvement of a polarized intermediate for dissociation of IBD has been forwarded by Keefer and Andrews (23). Keefer and Andrews observed that dissociation of IBD was immeasurably slow in carbon tetrachloride at 25° in darkness without an ionic catalyst. When a catalyst (iodine monochloride) was employed, however, IBD rapidly became equilibrated with iodobenzene and chlorine by a reaction that was found to be second order in catalyst.

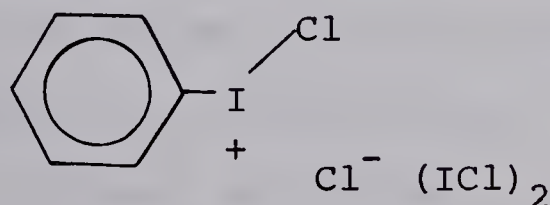


The dissociation constants, as defined in equation 2, were determined for reactions at 25 and 45° and are given below:

$$K = \frac{k_1}{k_2} = \frac{[\text{C}_6\text{H}_5\text{I}][\text{Cl}_2]}{[\text{C}_6\text{H}_5\text{ICl}_2]} \quad (2)$$

$$K_{25^\circ} = 2.2 \times 10^{-2} \text{ mole/l.}; K_{45^\circ} = 6.1 \times 10^{-2} \text{ mole/l.}$$

Very low activation energies were derived from the results of IBD dissociation reactions ($E_d = 0-4$ kcal/mole), and small, but negative activation energies were determined for the formation reactions of IBD ($E_f = -3$ to -8 kcal/mole). The observation of very low or negative activation energies for reactions involving halogens in solvents of low polarity indicates that the reactions are of high molecularity. Since the reactions involved in the formation and dissociation of IBD do not normally undergo reactions of high molecularity, a highly complexed reaction intermediate is expected to exist. Presumably IBD in a partially ionized form, as shown below, is the intermediate involved in the foregoing reactions.



An investigation was carried out into the effects of solvent changes on the dissociation constants and on the rates of dissociation and formation of IBD (24). Keefer and Andrews observed increases in the dissociation

constants for IBD dissociations at 25° in darkness as the solvent polarity was decreased in the following order: nitromethane, acetic acid, carbon tetrachloride. The dissociation constants observed in these solvents were as follows: $K_{\text{CH}_3\text{NO}_2} = 4 \times 10^{-4}$; $K_{\text{HOAc}} = 20 \times 10^{-4}$; $K_{\text{CCl}_4} = 200 \times 10^{-4}$ mole/l. The order of the dissociation constants listed above indicated that the dissociation products of IBD are less polar than IBD itself. The rates of formation and dissociation of IBD increased as the solvating efficiency of the solvent increased, i.e., in the order carbon tetrachloride, nitromethane, acetic acid; hence supporting the proposal that the dissociation and formation of IBD proceed via a polarized activated complex.

Method of Investigation

Evidence presented by McCombie et al. (5, 6, 7), Ingold (8), and by Keefer and Andrews (23, 24) suggests that rearrangement of IBD at elevated temperatures in darkness takes place by an intermolecular ionic reaction. The observations of Tanner and Gidley (1) regarding oxygen inhibited reactions at elevated temperatures in darkness also indicate that ionic mechanisms determine the products of IBD rearrangements. Otherwise, under de-oxygenated reaction conditions, free-radical reactions

of IBD with substrate predominate. The results obtained by Tanner and Van Bostelen (2) indicate that photo-initiated rearrangements of IBD at low temperatures are solely radical reactions.

In order to ascertain the mechanism or mechanisms involved in IBD rearrangements, samples of IBD were decomposed in sealed, evacuated reaction vessels which contained carbon tetrachloride as an inert liquid reaction medium. The products of IBD rearrangement, presumably by a free-radical reaction, were determined by carrying out photoinitiated decompositions at low temperatures. Products of thermally induced decompositions in the absence of light were also determined. A comparison of the products from photoinitiated decompositions with those detected from decompositions in darkness at elevated temperatures provided some insight into the mechanistic differences between thermally induced and photoinitiated rearrangements of IBD.

Decompositions of IBD were carried out under the aforementioned reaction conditions in the presence of free-radical inhibitors in order to demonstrate the importance of chain processes in the mechanism for rearrangement of IBD.

Iodobenzene dichloride was decomposed in solvents containing toluene and benzene. Both benzene and toluene

effectively solvate electrophilic intermediates by formation of π complexed species. If the rearrangement proceeds via an intermolecular process, either the stabilizing and/or steric effects of solvent complexed intermediates should alter the proportions of rearrangement products observed. Therefore, comparison of the products obtained from the decompositions in solvents containing the added substrates with those observed from decompositions in carbon tetrachloride alone will demonstrate if the rearrangement of IBD itself is an intermolecular reaction.

RESULTS

Unless otherwise stated, the results discussed below are from reactions in which 98-100% pure (by iodometric titration) IBD was decomposed in sealed, degassed, Pyrex ampules. Normally 1.1 mmole (0.1 g per ml solvent) of IBD were decomposed in each individual reaction. Anhydrous carbon tetrachloride was generally employed as a solvent. All decompositions at low temperatures in carbon tetrachloride were carried out as heterogeneous reaction mixtures containing solid IBD.

Organic products were quantitatively analysed by glpc on 10" x 1/4" SE-30 columns. Unreacted active chlorine (and molecular iodine) and hydrogen chloride were determined by iodometric titration. The percent decomposition of IBD was calculated from the titrimetric data as described on p. 93 in the Experimental section.

The Stability of IBD in Carbon Tetrachloride

Decompositions of IBD were carried out in order to determine the thermal stability of IBD in carbon tetrachloride and to examine the effect of irradiation on IBD in that solvent alone. Decomposition experiments also were conducted in carbon tetrachloride containing anhydrous hydrogen chloride in order to verify a suspected hydrogen chloride enhancement of IBD decompositions.

The results listed in Table I are correlations between reaction time and percent reaction observed for the

TABLE I

REACTION TIMES FOR DECOMPOSITION OF IBD IN CARBON TETRACHLORIDE

Reaction ^a Conditions	Time (Weeks)	Percent ^b Reaction	Percent Reaction per Week ($\times 10^2$)
0°, dark	6.5	16 ± 2 (2) ^c	0.02
0°, dark ^d	2.1	12 ± 4 (2)	0.06
26 - 28°, dark	15	46 ± 1 (2)	0.03
40°, dark	3.5	59 ± 2 (2)	0.17
40°, dark	7.5	90 ± 1 (2)	0.12
75°, dark	0.71	77 ± 2 (3)	1.10
0°, hv ^e	1.34	83 ± 4 (8)	0.62
0°, hv ^e	0.59	83 ± 4 (8)	1.41
0°, hv ^f	0.21	83 ± 2 (3)	3.96
40°, hv	0.16	81 ± 1 (3)	5.07

^a Reactions were carried out in sealed, degassed ampules.

^b Percents of reaction were determined in this and all following tables by the method described on p. 93.

^c Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^d The solvent contained 0.18 M anhydrous hydrogen chloride.

^e The large difference in reaction times is due to differences in experimental conditons. Specifically, different irradiation sources were used (see p. 84).

^f The reaction mixtures contained 0.22 mmole IBD per ml solvent; all others contained 0.37 mmole IBD per ml solvent.

decompositions of IBD in carbon tetrachloride. The values listed in the fourth column (Percent Reaction per Week) are convenient parameters used to compare the relative amounts of decomposition that occurred per unit time under the various reaction conditions. No kinetic investigations were carried out, therefore, only large differences between the values listed in column four are significant. For example, the small differences between the first three values reported indicate that decomposition of IBD is negligible at low temperature in darkness, even in the presence of hydrogen chloride. Comparison of the values presented for reactions at low temperatures in darkness with those for reactions at elevated temperatures in darkness and with those for irradiated reactions under all conditions demonstrate the necessity for thermal- and/or photoinitiation of the decomposition of IBD. The data presented in Tables III, IV, VII, IX, and XI, all of which are identical in form to Table I, also were examined with the understanding that only large differences between values given under the heading "Percent Reaction per Week" were significant.

Light initiated decompositions of heterogeneous mixtures of IBD in carbon tetrachloride were studied extensively at 0°. Reaction times were dependent on the quantity of IBD in the reaction mixtures and the light incident on the ampules. Even though the times

required for irradiated decomposition of IBD in carbon tetrachloride at 0° varied, the slowest observed reaction proceeded 25 times faster than decompositions in darkness at 0°. Photoinitiated decompositions of IBD at 40° were 30-40 times faster than decompositions at 40° in darkness.

Products of IBD Rearrangement in Carbon Tetrachloride

Products from decompositions of IBD in carbon tetrachloride which were carried at 0 or 40° with irradiation, as well as at 40 or 75° in darkness are listed in Table II as fractional yields based on the initial moles of IBD present in reaction mixtures.

Material balances were obtained which accounted for $87 \pm 2\%$ of both the phenyl and iodine initially present as IBD. Only $75 \pm 6\%$ of the original chlorine was accounted for in the rearrangement products.

Major components of the rearrangement products are listed below as relative percents of the total products reported in Table II, excluding unreacted active chlorine: hydrogen chloride ($\sim 40\%$), iodobenzene (I) (7-17%), 2-chloriodobenzene (II) (13-17%), and 4-chloriodobenzene (III) (10-25%). Considerably smaller percentages of ring dichlorinated iodobenzene (2-7%), molecular iodine (2-6%), chlorobenzene (2-5%), 1,4-dichlorobenzene (2-6%), 1,2-dichlorobenzene ($\sim 2\%$), and 3-chloriodobenzene ($\sim 1\%$) were detected also.

TABLE II
PRODUCTS FROM DECOMPOSITION OF IBD IN CARBON TETRACHLORIDE

REACTION CONDITIONS	0°, $h\nu$ (6) ^{a, b}	40°, $h\nu$ (3)	40°, DARK (2)	75°, DARK (3)
PRODUCTS	YIELD (MOLE / MOLE IBD)			
HCl	0.527 ± 0.035	0.578 ± 0.008	0.550 ± 0.102	0.563 ± 0.061
PhI ^c	0.231 ± 0.013	0.193 ± 0.005	0.196 ± 0.031	0.109 ± 0.004
2-ClC ₆ H ₄ I	0.221 ± 0.022	0.230 ± 0.005	0.215 ± 0.015	0.174 ± 0.037
4-ClC ₆ H ₄ I	0.134 ± 0.003	0.168 ± 0.004	0.327 ± 0.030	0.230 ± 0.010
Cl ₂ C ₆ H ₄ I ^d	0.057 ± 0.002	0.055 ± 0.004	TRACE	0.025 ± 0.009
I ₂	0.063 ± 0.005	0.071 ± 0.005	0.030 ± 0.007	0.038 ± 0.005
PhCl	0.029 ± 0.004	0.048 ± 0.002	TRACE	0.063 ± 0.003
p-Cl ₂ C ₆ H ₄	0.053 ± 0.016	0.070 ± 0.002	0.029 ± 0.007	0.084 ± 0.004
o-Cl ₂ C ₆ H ₄	0.027 ± 0.003	0.027 ± 0.001	0.030 ± 0.005	0.029 ± 0.002
3-ClC ₆ H ₄ I	0.007 ± 0.000	0.004 ± 0.000	-----	-----
UNREACTED ACTIVE CHLORINE	0.211 ± 0.007	0.222 ± 0.011	0.156 ± 0.035	0.255 ± 0.023
II / III	1.65 ± 0.16	1.35 ± 0.02	0.66 ± 0.00	0.76 ± 0.02

TABLE II

(continued)

^a Four of the six reaction mixtures contained 0.37 mmole IBD per ml solvent; the remaining two contained 0.22 mmole IBD per ml solvent.

^b Numbers in parentheses are the number of individual reactions that were carried out. The errors reported are standard deviations from the mean values reported.

^c The reported values for iodobenzene are quantities resulting from IBD rearrangement only. The total amount of iodobenzene detected is the sum of the reported quantity of iodobenzene and one-half of the value reported for unreacted active chlorine.

^d Molar values for $\text{Cl}_2\text{C}_6\text{H}_3\text{I}$ were estimated from the area ratio of product/freon.

The tendency for the mole ratios of 2-chloriodobenzene/4-chloriodobenzene (II/III) to be larger in the products from irradiated decompositions than in those from non-irradiated decompositions was a striking feature observed in the tabulation of IBD decomposition products. The ratio of II/III in the products from irradiated decompositions of IBD in carbon tetrachloride at 40° was 51% larger than that observed in the products from non-irradiated decompositions at 40° (1.34 compared with 0.66). The ratio of II/III found in the products from irradiated decomposition of IBD at 0° was even greater (1.65) than that observed in the products from irradiated decompositions at 40°.

3-Chloriodobenzene was not always detected in the decomposition products. The largest proportion (0.7%) of 3-chloriodobenzene was found when IBD underwent irradiated decomposition at 0°. The relative percent of 3-chloriodobenzene present in the total products from irradiated decomposition of IBD at 40° was approximately one-half of that observed in reactions at 0° with illumination. No 3-chloriodobenzene was detected in the products from decompositions of IBD at either 40 or 75° in darkness.

Although the exact isomeric composition of the ring dichlorinated iodobenzenes is uncertain, the major

component appeared to be a 1,2,4-trisubstituted benzene (see p. 102 in the Experimental section). A minor component (<50% of the major component), apparently a 1,2,3-trisubstituted benzene, was also detected. No product corresponding to a 1,3,5-trisubstituted benzene was detected.

IBD Decompositions in the Presence of Inhibitors

In order to determine the importance of free-radical reaction schemes in the rearrangement of IBD, the dichloride was decomposed at 0° with irradiation and at 40° in darkness in the presence of various free-radical inhibitors. Decompositions of heterogeneous mixtures of IBD (0.22 to 0.37 mmole IBD per ml solvent) in carbon tetrachloride were carried out in sealed, degassed ampules. The reaction mixtures also contained three mole percent of either p-hydroquinone (HQ), 1,3,5-trinitrobenzene (TNB), or 2,6-di-t-butyl-p-cresol (DTBC) all of which are free-radical inhibitors. Iodobenzene dichloride also was decomposed in sealed ampules containing atmospheric amounts of oxygen. Correlations between reaction time and percent decomposition for decompositions of IBD in reaction mixtures containing the aforementioned free-radical inhibitors are given in Table III. As is evident from a comparison of the reaction times for decompositions in

TABLE III
REACTION TIMES FOR DECOMPOSITION OF IBD IN
THE PRESENCE OF FREE-RADICAL INHIBITORS

Inhibitors	Reaction Conditions	Time (Weeks)	Percent Reaction	Percent Reaction per Week ($\times 10^2$)
None ^a	0°, hv	0.2	83 $\pm$ 2 (3) ^f	3.96
None ^a	40°, dark	3.5	59 $\pm$ 2 (2)	0.17
Oxygen ^{a,b}	0°, hv	0.4	42 $\pm$ 2 (2)	1.05
Oxygen ^{a,b}	0°, hv	1.3	86 $\pm$ 3 (3)	0.66
Oxygen ^{a,b}	40°, dark	7.5	55 $\pm$ 1 (2)	0.07
DTBC ^c	0°, hv	0.2	85 $\pm$ 1 (3)	4.25
DTBC ^c	40°, dark	4.0	60 $\pm$ 1 (2)	0.15
TNB ^d	0°, hv	0.4	79 $\pm$ 1 (2)	1.98
TNB ^d	40°, dark	0.4	28 (1)	0.07
TNB ^d	40°, dark	12.7	84 (1)	0.07
HQ ^e	0°, hv	0.4	79 $\pm$ 1 (3)	1.98
HQ ^e	40°, dark	0.4	24 (1)	0.07
HQ ^e	40°, dark	12.7	86 $\pm$ 2 (2)	0.07

TABLE III

(continued)

- ^a Reaction mixtures contained 0.37 mmole IBD per ml solvent.
- ^b Reactions designated by ^b were carried out in sealed, but non-degassed ampules; all others were carried out in degassed ampules.
- ^c The reaction mixtures contained 2,6-di-t-butyl-p-cresol in concentrations of 6.5×10^{-3} M, and 0.22 mmole IBD per ml solvent.
- ^d The reaction mixtures contained sym-trinitrobenzene in concentrations of 7.6×10^{-3} M, and 0.24 mmole IBD per ml solvent.
- ^e The reaction mixtures contained p-hydroquinone in concentrations of 7.3×10^{-3} M, and 0.24 mmole IBD per ml solvent.
- ^f Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

the presence of inhibitors with those for decompositions without inhibitors, none of the inhibitors used has any significant retarding effect on the decomposition of IBD under irradiated conditions at 0°. Although the ratio of percent decomposition/reaction time varied somewhat for different sets of experiments, the ratios for reactions containing inhibitors and simultaneously decomposed control reactions without inhibitors were in agreement.

Atmospheric amounts of oxygen, three mole percent TNB, or three mole percent HQ did not significantly decrease the amount of IBD decomposition observed per unit time in reactions that were carried out at 40° in darkness. The inhibitor DTBC had no effect on the time required for decomposition of IBD at 40° in darkness.

Effect of Inhibitors on Products from IBD Decompositions

In order to examine the effect of inhibitors on the products from IBD decompositions, the products were examined from reactions in which the dichloride was decomposed in the presence of various inhibitors at 40° in darkness and at 0° with irradiation. Except for reactions in which atmospheric oxygen was used as an inhibitor, all decompositions were carried out in degassed, sealed ampules. The products from decompositions of IBD in the presence of the inhibitors are reported in Table IV (40°, in darkness) and Table V (0° with irradiation) as fractional yields relative to the initial

TABLE IV

PRODUCTS FROM PHOTOINITIATED DECOMPOSITION OF IBD AT 0° IN THE
 PRESENCE OF FREE-RADICAL INHIBITORS IN CARBON TETRACHLORIDE ^a

Inhibitor	Oxygen (2) ^b	HQ (3)	TNB (3)	DTBC (3)	None (6)
Product	Yield (mole / mole IBD)				
HCl	0.552	0.583	0.602	0.395	0.527
PhI	0.170	0.173	0.238	0.356	0.231
2-ClC ₆ H ₄ I	0.235	0.264	0.295	0.229	0.221
4-ClC ₆ H ₄ I	0.154	0.149	0.171	0.130	0.134
Cl ₂ C ₆ H ₃ I	0.054	0.071	0.101	0.044	0.057
I ₂	0.044	0.077	0.092	0.065	0.063
PhCl	0.022	0.049	0.040	0.036	0.029
1,4-Cl ₂ C ₆ H ₄	0.045	0.080	0.094	0.063	0.053
1,2-Cl ₂ C ₆ H ₄	0.023	0.022	0.025	0.034	0.027
3-ClC ₆ H ₄ I	0.007	0.009	0.011	0.007	0.007
Unreacted Active Chlorine	0.304	0.251	0.225	0.183	0.211
II / III	1.53	1.77	1.72	1.79	1.65

^a See Table III (p. 28) for exact reaction conditions.

^b Numbers in parentheses are the number of individual reactions that were carried out.

TABLE V

PRODUCTS FROM THERMOLYSIS OF IBD AT 40° IN THE PRESENCE OF
FREE-RADICAL INHIBITORS IN CARBON TETRACHLORIDE^a

Inhibitor	Oxygen (2) ^b	HQ (3)	TNB (3)	None (2)
Product	Yield (mole / mole IBD)			
HCl	0.410	0.562	0.579	0.560
PhI	0.129	0.167	0.145	0.196
2-ClC ₆ H ₄ I	0.213	0.244	0.227	0.215
4-ClC ₆ H ₄ I	0.325	0.350	0.369	0.327
Cl ₂ C ₆ H ₃ I	0.030	0.048	0.047	trace
I ₂	0.012	0.059	0.056	0.030
PhCl	-----	0.022	0.025	trace
1,4-Cl ₂ C ₆ H ₄	0.024	0.075	0.069	0.029
1,2-Cl ₂ C ₆ H ₄	0.010	0.021	0.026	0.030
Unreacted Active Chlorine	8.62	0.562	0.171	0.156
II / III	0.65	0.72	0.61	0.66

^a See Table III (p. 28) for exact reaction conditions.

^b Numbers in parentheses are the number of individual reactions that were carried out.

amounts of IBD in the reaction mixtures. Material balances were obtained which accounted for $100 \pm 10\%$ of both the initial phenyl and iodine, and for $85 \pm 10\%$ of the initial chlorine that were present in the reaction mixtures as IBD.

The mole ratios of II/III observed in the products from light induced decompositions of IBD at 0° in the presence of inhibitors are included in Table IV. The mean value obtained (1.70 ± 0.09) is in agreement with the mole ratio for II/III (1.65 ± 0.16 ; from Table II, p. 23) observed in the products from photoinitiated decompositions of IBD at 0° in the absence of inhibitors. The mean value for the mole ratio of II/III (0.66 ± 0.04) observed in the products from decompositions in the presence of inhibitors at 40° in darkness (Table V), corresponds with that reported (0.65 ; from Table II, p. 23) in the products from thermal decomposition of IBD at 40° in the absence of inhibitors.

Relative percent yields were calculated for the rearrangement products, excluding unreacted active chlorine, from decompositions of IBD in the presence of inhibitors. Mean values of the relative yields obtained in that manner are compared in Table VI with relative yields which had been similarly calculated for products from decompositions of IBD in the absence of

TABLE VI
MEAN VALUES OF RELATIVE YIELDS OF PRODUCTS FROM IBD
DECOMPOSITIONS IN THE PRESENCE OF INHIBITORS ^a

Products	Relative Yield (%) From Decompositions at 0°	Relative Yield (%) From Decompositions at 40°
HCl	36.7 ± 4.1 (39.7) ^b	36.5 ± 0.7 (40.8)
PhI	16.2 ± 5.1 (16.6)	10.5 ± 0.7 (13.2)
2-ClC ₆ H ₄ I	17.3 ± 0.6 (16.7)	16.3 ± 1.3 (15.7)
4-ClC ₆ H ₄ I	10.4 ± 0.7 (10.1)	24.9 ± 2.2 (24.9)
Cl ₂ C ₆ H ₃ I	4.5 ± 0.9 (4.3)	2.9 ± 0.2 ----
I ₂	4.7 ± 0.7 (4.3)	2.9 ± 1.0 (2.2)
PhCl	2.5 ± 0.4 (2.2)	1.5 ± 0.1 ---
1,4-Cl ₂ C ₆ H ₄	4.8 ± 0.7 (4.0)	3.8 ± 1.1 (2.1)
1,2-Cl ₂ C ₆ H ₄	1.8 ± 0.4 (2.0)	1.3 ± 0.3 (2.2)
3-ClC ₆ H ₄ I	0.6 ± 0.1 (0.5)	----- ---

^a Refer to Table III (p.28) for exact reaction conditions.

^b Numbers in parentheses are the relative yields of products from decompositions of IBD in the absence of inhibitors. Refer to Table II (p. 23) for exact reaction conditions.

inhibitors (Table II, p. 23). Although the standard deviations are substantial in some instances, the mean values reported for relative yields of products from reactions in the presence of inhibitors coincided reasonably with those reported for products from decompositions of IBD under corresponding reaction conditions without inhibitors.

Effects of Solvent Changes on IBD Decomposition

Decompositions of IBD (0.37 mmole per ml solvent) were carried out in 100% benzene, and in solvents composed of either 0.61 M toluene or 0.63 M benzene in carbon tetrachloride. These reactions were carried out at 0° with irradiation and at 40° in darkness to ascertain what effect variations of solvents will have on the rearrangement of IBD.

Decomposition of IBD in Carbon Tetrachloride Containing 0.61 M Toluene

Reaction times required for the disappearance of heterogeneous mixtures of IBD (0.37 mmole per ml solvent) in carbon tetrachloride containing 0.61 M toluene are given in Table VII. Comparison of the ratios for percent decomposition per week reported for decomposition of IBD at 40° in the presence of toluene with those reported for decompositions in carbon tetrachloride

TABLE VII
REACTION TIMES FOR DECOMPOSITIONS OF IBD IN CARBON
TETRACHLORIDE CONTAINING 0.61 M TOLUENE ^c

Reaction Conditions	Time (Weeks)	Percent Reaction	Percent Reaction per Week ($\times 10^2$)
0°, dark	2.0	28 $\pm$ 1 (3) ^a	0.14
0°, hv	0.15	95 $\pm$ 2 (3)	6.33
40°, dark	0.65	90 $\pm$ 0 (3)	1.39
40°, hv	0.02	98 $\pm$ 0 (3)	49.0
0°, dark ^b	6.5	16 $\pm$ 2 (2)	0.03
0°, hv ^b	0.59	83 $\pm$ 4 (8)	1.41
40°, dark ^b	7.50	90 $\pm$ 1 (2)	0.12
40°, hv ^b	0.16	81 $\pm$ 1 (3)	5.07

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b Taken from Table I (p. 20) for reactions in carbon tetrachloride.

^c Reaction mixtures contained 0.37 mmole IBD per ml solvent.

indicates that toluene effected a ten-fold enhancement in the values observed for the percent decomposition per week. A similar comparison of reaction times for irradiated decompositions of IBD that were carried out at 0° shows that the presence of toluene caused a four-fold increase in the observed ratio for percent decompositions per week. The value obtained for the percent decomposition per week from non-irradiated reactions containing toluene at 0° was five times greater than that obtained from reactions without toluene.

Products obtained from decompositions of the heterogeneous mixtures of IBD in solvent composed of 0.61 M toluene in carbon tetrachloride are presented in Table VIII as fractional yields based on initial amounts of IBD in reaction mixtures. Material balances were obtained for both molecular iodine and phenyl which accounted for $95 \pm 4\%$ of the material initially present as IBD. However, only $70 \pm 5\%$ of the initial chlorine was accounted for in the products.

Decompositions of IBD in solvent containing toluene proceeded with 40-60% (mole/mole IBD) chlorination of toluene resulting in formation of benzyl chloride (IV) and ring chlorinated toluene (V). Iodobenzene 70-75% (mole/mole IBD) and hydrogen chloride 60-65% (mole/mole IBD) were other predominant products observed.

TABLE VIII

PRODUCTS FROM DECOMPOSITION OF IBD IN CARBON
TETRACHLORIDE CONTAINING 0.61 M TOLUENE

Reaction Conditions	0°, hv (3) ^a	40°, hv (3)	40°, dark (3)
Product	Yield (mole / mole IBD)		
HCl	0.65 ± 0.18	0.65 ± 0.04	0.62 ± 0.02
PhI	0.65 ± 0.02	0.74 ± 0.04	0.73 ± 0.01
C ₆ H ₅ CH ₂ Cl	0.29 ± 0.01	0.40 ± 0.05	0.09 ± 0.00
ClC ₆ H ₄ CH ₃ ^b	0.21 ± 0.01	0.19 ± 0.01	0.30 ± 0.01
2-ClC ₆ H ₄ I	0.10 ± 0.01	0.08 ± 0.01	0.07 ± 0.00
4-ClC ₆ H ₄ I	0.08 ± 0.01	0.14 ± 0.01	0.14 ± 0.00
3-ClC ₆ H ₄ I	0.01 ± 0.00	-----	-----
Unreacted ^c Active Chlorine	0.09 ± 0.04	0.05 ± 0.00	0.03 ± 0.00
II / III	1.14 ± 0.08	0.58 ± 0.00	0.53 ± 0.02

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b The product reported for ClC₆H₄CH₃ is a 55 : 45 mixture of 2-chlorotoluene ; 4-chlorotoluene.

^c A visually detectable trace of molecular iodine is included in the value reported for unreacted active chlorine.

Only 18-23% (mole/mole IBD) yields of chlorinated iodobenzene were detected in the products. Neither chlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene, nor ring-dichlorinated iodobenzene were detected by the analytical methods employed.

Mole ratios of II/III observed in products from decompositions of IBD in the presence of toluene deviated somewhat from values obtained from IBD decompositions in carbon tetrachloride alone. However, since the mole ratios of II/III are of special consideration, they will be discussed separately below (p. 47).

As expected, the mole ratios of benzyl chloride/ring-chlorinated toluene (IV/V) was found to be larger for irradiated reactions (1.37 at 0° and 2.04 at 40°) than for non-irradiated reactions (0.31 at 40°). Further examination by differential infrared analysis disclosed that the ring-chlorinated toluene (V) resulting from reactions at 40° was a 55:45 mixture of 2-chlorotoluene:4-chlorotoluene. Compound V isolated from reaction mixtures in which IBD had been photolytically decomposed at 0° appeared to be a 70:30 mixture of ortho:para chlorotoluenes.

Decomposition of IBD in Carbon Tetrachloride Containing
0.63 M Benzene

Reaction times for decompositions of heterogeneous mixtures of IBD (0.37 mmole per ml solvent) in carbon tetrachloride containing 0.63 M benzene were correlated with their respective percents of decomposition and reported in Table IX. Comparison of the ratios of percent decomposition per week reported for decompositions of IBD in the presence of benzene with those reported for decompositions in carbon tetrachloride alone indicates that inclusion of 0.63 M benzene failed to alter the time required for decomposition of IBD significantly.

The ratios observed for percent decomposition per week from photoinitiated decompositions of IBD at 0° in 0.63 M benzene, however, were somewhat smaller (48%/wk.) than ratios for corresponding reactions in carbon tetrachloride (67%/wk.).

Products from decompositions of the heterogeneous mixtures of IBD in carbon tetrachloride containing 0.63 M benzene are reported in Table X as fractional yields based on the initial amounts of IBD in the reaction mixtures. Material balances were obtained which accounted for $98 \pm 1\%$ of the iodine and $73 \pm 2\%$ of the chlorine present in the initial reaction mixtures as IBD. The material balances obtained for iodine and chlorine

TABLE IX
REACTION TIMES FOR DECOMPOSITION OF IBD IN CARBON
TETRACHLORIDE CONTAINING 0.63 M BENZENE ^c

Reaction Conditions	Time (Weeks)	Percent Reaction	Percent Reaction per Week ($\times 10^2$)
0°, hv	2.1	96 $\pm$ 0 (3) ^a	0.46
40°, dark	3.6	75 (1)	0.21
40°, dark	13.1	94 (1)	0.07
40°, hv	0.16	90 $\pm$ 2 (4)	5.63
0°, dark ^b	6.5	16 $\pm$ 2 (2)	0.03
0°, hv ^b	1.34	83 $\pm$ 4 (8)	0.62
40°, dark ^b	7.50	90 $\pm$ 1 (2)	0.12
40°, hv ^b	0.16	81 $\pm$ 1 (3)	5.07

^a Numbers in parentheses indicate the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b Taken from Table I (p. 20) for reactions in carbon tetrachloride.

^c Reaction mixtures contained 0.37 mmole IBD per ml solvent.

corresponded with those normally observed, but an abnormally high material balance of $124 \pm 3\%$ was observed for the phenyl that was initially present in the reaction mixtures.

Examination of Table X reveals that chlorobenzene was formed in yields which were five times in excess of those normally observed in products from IBD decomposition in carbon tetrachloride. Chlorobenzene was detected in approximately $25 \pm 5\%$ (mole/mole IBD) yields. The chlorobenzene formed is equivalent to $15 \pm 2\%$ of the reaction products based on the total products, excluding unreacted active chlorine, that were detected. The remainder of the products detected, expressed as relative yields of products, were composed mainly of hydrogen chloride ($34 \pm 2\%$), iodobenzene ($27 \pm 2\%$), 2-chloriodobenzene ($7 \pm 1\%$) and 4-dichlorobenzene ($8 \pm 1\%$). Ring-dichlorinated iodobenzene, molecular iodine, 1,4-dichlorobenzene, 1,2-dichlorobenzene, and 3-chloriodobenzene were all detected in relative yields of 0.5-3%. Total yields of 2-chloriodobenzene and 4-chloriodobenzene were slightly lower in the products from decompositions of IBD in the presence of benzene than those from decompositions in carbon tetrachloride alone.

TABLE X
 PRODUCTS FROM DECOMPOSITION OF IBD IN CARBON
 TETRACHLORIDE CONTAINING 0.63 M BENZENE

Reaction Conditions	0°, hν (3) ^a	40°, hν (3)	40°, dark (2)
Product	Yield (mole / mole IBD)		
HCl	0.71 ± 0.03	0.64 ± 0.04	0.46 ± 0.03
PhI	0.55 ± 0.02	0.48 ± 0.03	0.39 ± 0.03
2-ClC ₆ H ₄ I	0.14 ± 0.01	0.15 ± 0.01	0.08 ± 0.01
4-ClC ₆ H ₄ I	0.16 ± 0.01	0.14 ± 0.01	0.14 ± 0.01
Cl ₂ C ₆ H ₃ I	0.03 ± 0.00	0.05 ± 0.00	0.05 ± 0.00
I ₂	0.05 ± 0.00	0.06 ± 0.00	0.04 ± 0.00
PhCl	0.24 ± 0.01	0.33 ± 0.01	0.20 ± 0.03
1,4-Cl ₂ C ₆ H ₄	0.06 ± 0.00	0.06 ± 0.00	0.03 ± 0.00
1,2-Cl ₂ C ₆ H ₄	0.02 ± 0.00	0.03 ± 0.00	0.02 ± 0.00
3-ClC ₆ H ₄ I	0.01 ± 0.00	0.01 ± 0.00	-----
Unreacted Active Chlorine	-----	0.08 ± 0.01	0.48 ± 0.03
II / III	0.89 ± 0.01	1.05 ± 0.03	0.60 ± 0.05

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

Mole ratios of II/III were altered somewhat by inclusion of benzene into the solvent for IBD decompositions. Since the mole ratios of II/III are of special interest, they are discussed separately below (p. 47).

Decomposition of IBD in Benzene

Reaction times for decompositions of IBD in 100% benzene are listed in Table XI with the corresponding percents of decomposition that were observed. Reaction mixtures contained 0.37 mmole IBD per ml solvent. At low temperature the reaction mixtures were heterogeneous but at 40° the IBD present was completely in solution. A three-fold rate enhancement of the value for the percent decomposition per week was observed when benzene was used as a solvent for non-irradiated reactions at 0°. The greatest enhancement was observed for non-irradiated decompositions at 40°. In that instance, decomposition of IBD was thirty times faster than those in carbon tetrachloride.

One set of reactions was carried out in the presence of 0.37 M anhydrous hydrogen chloride in order to determine the extent of a suspected hydrogen chloride catalysed ionic decomposition of IBD at 0° in darkness. The value obtained for the ratio of percent decomposition per week in the presence of added hydrogen chloride was twice that observed in

TABLE XI

REACTION TIMES FOR DECOMPOSITION OF IBD IN BENZENE^d

Reaction Conditions	Time (Weeks)	Percent Reaction	Percent Reaction per Week ($\times 10^2$)
0°, dark	3	25 (1) ^a	0.08
0°, dark	4	33 (1)	0.08
0°, dark ^b	1.5	24 $\pm$ 1 (3)	0.16
0°, hv	0.2	99 $\pm$ 2 (4)	4.95
40°, dark	0.26	91 $\pm$ 1 (3)	3.50
40°, hv	0.04	95 $\pm$ 2 (4)	22.8
0°, dark ^c	6.5	16 $\pm$ 2 (2)	0.03
0°, hv ^c	0.59	83 $\pm$ 4 (8)	1.41
40°, dark ^c	7.50	90 $\pm$ 1 (2)	0.12
40°, hv ^c	0.16	81 $\pm$ 1 (3)	5.07

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b The solvent contained 0.37 M anhydrous hydrogen chloride.

^c Taken from Table I (p. 20) for reactions in carbon tetrachloride.

^d Reaction mixtures contained 0.37 mmole IBD per ml solvent.

reactions without added hydrogen chloride. However, the observed rate enhancement was not great enough to indicate that a hydrogen chloride catalysed ionic reaction was a significant competing reaction in opposition to the photoinitiated decomposition of IBD in benzene at 0°.

Products from decompositions of IBD in benzene at 0° with irradiation and 40° in darkness are presented in Table XII as fractional yields based on the initial IBD present in the reaction mixtures. Satisfactory material balances were obtained for iodine only. In that case, $98 \pm 3\%$ of the initial iodine was accounted for in the reaction products. The quantity of phenyl detected was $149 \pm 10\%$ of the phenyl initially present in the reaction mixtures as IBD. Only $64 \pm 2\%$ of the initial chlorine was accounted for in the reaction products.

Chlorobenzene was formed in anomalously large yields ($51 \pm 9\%$; mole/mole IBD). The chlorobenzene detected represented $25 \pm 4\%$ of the total products, excluding unreacted active chlorine, that were observed. Hydrogen chloride ($30 \pm 3\%$) and iodobenzene ($41 \pm 1\%$) were the only other predominant products that were detected. Very small relative amounts of 2-chloriodobenzene (1-3%) and 4-chloriodobenzene (1-2.5%) were observed. Trace amounts of 1,4-dichlorobenzene, but neither 1,2-dichlorobenzene nor

TABLE XII

PRODUCTS FROM DECOMPOSITION OF IBD IN BENZENE

Reaction Conditions	0°, h ν (2) ^{a,b}	40°, h ν (2)	40°, dark (2)
Product	Yield (mole / mole IBD)		
HCl	0.69 $\pm$ 0.02	0.65 $\pm$ 0.03	0.51 $\pm$ 0.02
PhI	0.79 $\pm$ 0.02	0.86 $\pm$ 0.02	0.91 $\pm$ 0.03
2-ClC ₆ H ₄ I	0.07 $\pm$ 0.00	0.03 $\pm$ 0.00	0.02 $\pm$ 0.00
4-ClC ₆ H ₄ I	0.05 $\pm$ 0.00	0.03 $\pm$ 0.00	0.02 $\pm$ 0.00
Cl ₂ C ₆ H ₃ I	0.04 $\pm$ 0.00	-----	-----
I ₂	0.02 $\pm$ 0.00	-----	-----
PhCl	0.37 $\pm$ 0.03	0.57 $\pm$ 0.03	0.60 $\pm$ 0.03
1,4-Cl ₂ C ₆ H ₄	0.02 $\pm$ 0.00	-----	-----
1,2-Cl ₂ C ₆ H ₄	trace	-----	-----
3-ClC ₆ H ₃ I	trace	trace	-----
Unreacted Active Chlorine	-----	0.07 $\pm$ 0.01	0.16 $\pm$ 0.02
II/III	1.34 0.06	1.03 $\pm$ 0.03	0.77 $\pm$ 0.02

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b Reactions were carried out at temperatures slightly higher than the melting point of benzene (5°).

ring-dichlorinated iodobenzene were detected in the products from decompositions of IBD in benzene.

The mole ratio of II/III observed in the products was curiously affected by the use of benzene as a solvent. The relationship between the ratios of II/III observed in products from decompositions of IBD in the various reaction media that were employed are presented in the following section.

Effects of Toluene and Benzene on Ratios of
2-Chloriodobenzene/4-Chloriodobenzene (II/III)

Mean values observed for the ratios of II/III in the products from decompositions of IBD (0.37 mmole per ml solvent) in either carbon tetrachloride, 0.61 M toluene or 0.63 M benzene in carbon tetrachloride, or in benzene are listed in Table XIII.

General examination of Table XIII reveals that ratios of II/III observed in products from irradiated reactions are considerably larger than those observed in products from non-irradiated decompositions. For decompositions at 40° in solvent containing 0.61 M toluene, however, the ratios of II/III observed in products from irradiated and non-irradiated decompositions of IBD are nearly identical. The ratios of II/III in products from reactions carried out under non-irradiated conditions (0.60 ± 0.05) are less variable than those

TABLE XIII

RATIOS OF 2-CHLOROIODOBENZENE / 4-CHLOROIODOBENZENE IN PRODUCTS FROM DECOMPOSITION OF IBD

Reaction Conditions	0°, hν	40°, hν	40°, dark
Solvent	Ratio of 2-Chloroiodobenzene / 4-Chloroiodobenzene		
Carbon Tetrachloride	1.63 ± 0.32 (14) ^a	1.34 ± 0.02 (3)	0.63 ± 0.03 (4)
0.61 M Toluene ^b	1.14 ± 0.08 (3)	0.58 ± 0.00 (3)	0.53 ± 0.02 (2)
0.63 M Benzene ^b	0.95 ± 0.04 (3)	1.05 ± 0.05 (3)	0.60 ± 0.04 (3)
Benzene	1.32 ± 0.12 (2)	1.03 ± 0.03 (3)	0.77 ± 0.02 (2)

^a Numbers in parentheses are the number of individual reactions that were carried out. Errors reported are standard deviations from the mean values reported.

^b The bulk of the solvent was composed of carbon tetrachloride.

observed in products from irradiated decompositions (1.13 ± 0.21). Also, except for decompositions in 0.63 M benzene, the ratios of II/III are larger in the products from irradiated decompositions at 0° than in those from irradiated decompositions in identical solvents at 40°.

The observed variations in ratios of II/III in the products from reactions under identical reaction conditions but in different solvents merit special consideration. Alterations of the solvents from pure carbon tetrachloride into either 0.61 M toluene or 0.63 M benzene in carbon tetrachloride, or into benzene effected 20-40% decreases in the observed ratios of II/III.

Three anomalies appeared within the correlation of changes in the ratios of II/III with solvent changes. Firstly, the ratio of II/III observed for irradiated decompositions of IBD in 0.61 M toluene at 40° is almost 60% smaller than that observed in carbon tetrachloride. Secondly, a large difference exists between the values observed for ratios of II/III in the products from irradiated decompositions of IBD at 0° in solvents containing benzene. The ratio of II/III observed in the products from decompositions in 100% benzene is within experimental error of that observed in carbon tetrachloride; whereas the ratio of II/III observed in

0.63 M benzene is substantially smaller (45 and 32% respectively) than those detected in carbon tetrachloride and benzene. Thirdly, the ratio of II/III observed in the products from decompositions of IBD in benzene at 40° without irradiation was 20% greater than that observed in the products from decompositions under identical conditions in carbon tetrachloride.

Decomposition of Solid IBD

In order to confirm the products from decomposition of solid IBD, samples of the solid dichloride were decomposed in sealed, evacuated ampules. Irradiation of solid IBD (0.76 mmole) at 0° resulted in an 87% loss of titer within 0.45 weeks. A sample of solid IBD (0.80 mmole) lost 95% of its initial titer for active halogen after being heated at 75° in darkness for 0.12 weeks. The resultant products, identified and quantitatively determined by the same methods previously described for decompositions in solvents, are presented in Table XIV as fractional yields, based on the quantities of IBD initially present in reaction mixtures. Approximately 90% of the material in the initial IBD was accounted for in analysis of products from either thermally induced or photoinitiated decompositions of solid IBD.

TABLE XIV

PRODUCTS FROM DECOMPOSITION OF SOLID IBD

Reaction Conditions	0°, hv	75°, dark
Product	Yield (mole / mole IBD)	
HCl	0.79	0.85
4-ClC ₆ H ₄ I	0.33	0.40
2-ClC ₆ H ₄ I	0.26	0.30
PhI	0.01	0.02
1,4-Cl ₂ C ₆ H ₄	0.05	0.02
Cl ₂ C ₆ H ₃ I	0.04	0.06
3-ClC ₆ H ₄ I	0.02	----
I ₂	0.03	0.01
Unreacted Active Chlorine	0.24	0.10
II / III	0.79	0.74

Decomposition of solid IBD both at 0° with irradiation and at 75° in darkness yielded almost identical product distributions, of which predominant members were hydrogen chloride (51%), 4-chloriodobenzene ($22 \pm 2\%$) and 2-chloriodobenzene ($17 \pm 1\%$). A surprisingly small amount of iodobenzene ($\sim 1\%$) was present as a minor component. Small amounts of 1,4-dichlorobenzene ($\sim 2\%$), ring-dichlorinated iodobenzene ($\sim 3\%$) and molecular iodine ($\sim 1\%$) were also detected.

Reactions of IBD with Polar Catalysts

A reaction between a 1:1:1 mixture of iodobenzene, IBD, and iodine monochloride (ICl) was carried out in order to determine the effect of ICl on decompositions of IBD. A blank reaction containing only iodobenzene and ICl was carried out concurrently. Both reactions were carried out at room temperature in darkness. Carbon tetrachloride was used as the solvent. The solid IBD initially present in the reaction mixture disappeared within 15 minutes and was accompanied by evolution of hydrogen chloride. Iodobenzene, 2-chloriodobenzene, and 4-chloriodobenzene were detected in glpc analysis of the final reaction mixture. The ratio of II/III was observed to be 0.7.

No apparent reaction occurred in the blank reaction mixture. Analysis of the final reaction mixture by glpc revealed that only traces of chlorinated iodobenzene were in the products.

Since iodine trichloride (ICl_3) was suspected to be an intermediate in the reaction between IBD and ICl , a reaction between ICl_3 and iodobenzene was carried out at room temperature in darkness. Carbon tetrachloride was used as the solvent. A precipitate, which appeared to be IBD, formed almost immediately after the reagents were mixed. The precipitate disappeared within one hour and was accompanied by evolution of hydrogen chloride. Analysis of the final reaction mixture by glpc revealed that iodobenzene, 2-chloriodobenzene, and 4-chloriodobenzene were the only products other than hydrogen chloride that were formed in the reaction. The ratio of II/III was 0.7.

DISCUSSION

Results of the initiation experiments demonstrate that reaction mixtures containing IBD in solvents of low polarity, which are inert to chlorination, are stable to loss of active chlorine unless subjected to irradiation. Inclusion of anhydrous hydrogen chloride into the reaction media failed to induce an appreciable non-irradiated decomposition of IBD at low temperatures. Upon heating to 40°, decomposition of IBD occurred in inert, non-polar solvents even without irradiation. Nearly identical product distributions were observed in both photoinitiated (0°) and thermally induced (40°) decompositions of IBD in carbon tetrachloride, except that the ratio of 2-chloriodobenzene/ 4-chloriodobenzene (II/III) and the yields of chlorobenzene were larger in the photoinitiated reactions than in non-irradiated reactions. The ratio of II/III observed in the products from photoinitiated decompositions of IBD at 40° was intermediate to that observed in the products from reactions at the condition extremes employed. Traces of 3-chloriodobenzene were observed in the products from irradiated reactions but no 3-chloriodobenzene was detected in the products from non-irradiated reactions.

Concluding from the variations observed in the product distributions, different mechanisms evidently are operative for irradiated and non-irradiated decompositions of IBD.

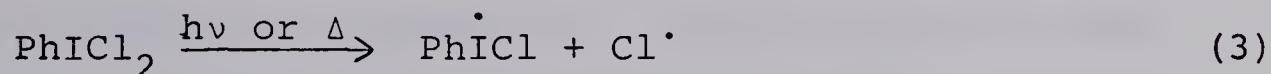
Quantitative formation of chlorobenzene by displacement of iodine from iodobenzene was observed when reactions between sulfuryl chloride and iodobenzene were carried out in the presence of traces of peroxides (25). All other chlorinations of iodobenzene using any other source of chlorine resulted in quantitative formation of IBD. Therefore, a mechanism in which iodobenzene is simply chlorinated by atomic chlorine or chloronium cations cannot be considered as a principal reaction scheme to account for the products observed from rearrangements of IBD.

Results of previous investigations (1,2) conclusively demonstrated that reactions between IBD and substrates are free-radical processes. Photo-initiation of the rearrangement itself, and the observation of chlorobenzene in the products from photoinitiated decompositions of IBD indicate that mechanisms involving free-radical intermediates are feasible for the photoinitiated rearrangement of IBD.

Anomalously large yields of chlorobenzene were detected in the products from decompositions of IBD in benzene and ring chlorinated toluenes were detected in

the products from reactions of IBD with toluene. The mechanisms for formation of chlorobenzene from benzene, and for formation of ring chlorinated toluenes are known ionic reactions. The foregoing experimental observations indicate that ionic processes also can be involved in the rearrangement of IBD.

The reaction schemes considered for homolytic decompositions of IBD can be grouped together either as intermolecular (Schemes V-VII) or intramolecular processes (Schemes VIII-IX). The initial step of all the homolytic reaction sequences depicted in Schemes V-IX is a photoinitiated or thermally induced homolytic cleavage of an I-Cl bond to form the phenylchloroiodinyl radical ($\text{Ph}\dot{\text{I}}\text{Cl}$) and atomic chlorine.

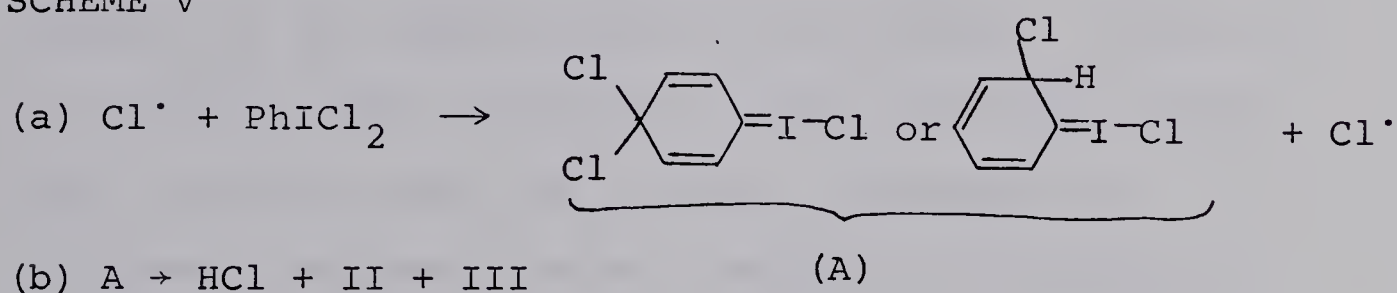


The initiation step (eq. 3) has been confirmed (1, 2, 18) and existence of the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical has been verified (2).

The intermolecular schemes were considered despite the fact that no evidence was available in support of mechanisms having chain processes of substantial length. An examination of the quantum yield for the disappearance of IBD was inconclusive, but the results indicated that the reaction sequences involved in the rearrangement of IBD had a chain length approaching unity (26).

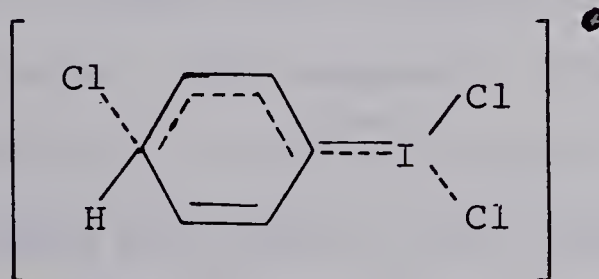
The intermolecular sequence depicted in Scheme V involves a direct attack of atomic chlorine on IBD by a 1,5- or 1,3- displacement of chlorine. Aromatization of the intermediate (A) formed in that manner results in liberation of hydrogen chloride and formation of either 2-chloriodobenzene (II) or 4-chloriodobenzene (III).

SCHEME V



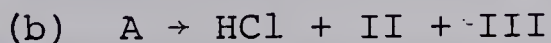
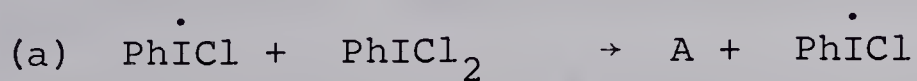
Formation of pi complexes between atomic chlorine and aromatic systems which are deactivated by electron withdrawing substituents is unfavorable (17).

Stabilization, by conjugation, of the transition state for the 1,3- or 1,5- displacement of atomic chlorine may sufficiently reduce the activation energy required in Va to render the displacement a feasible reaction.

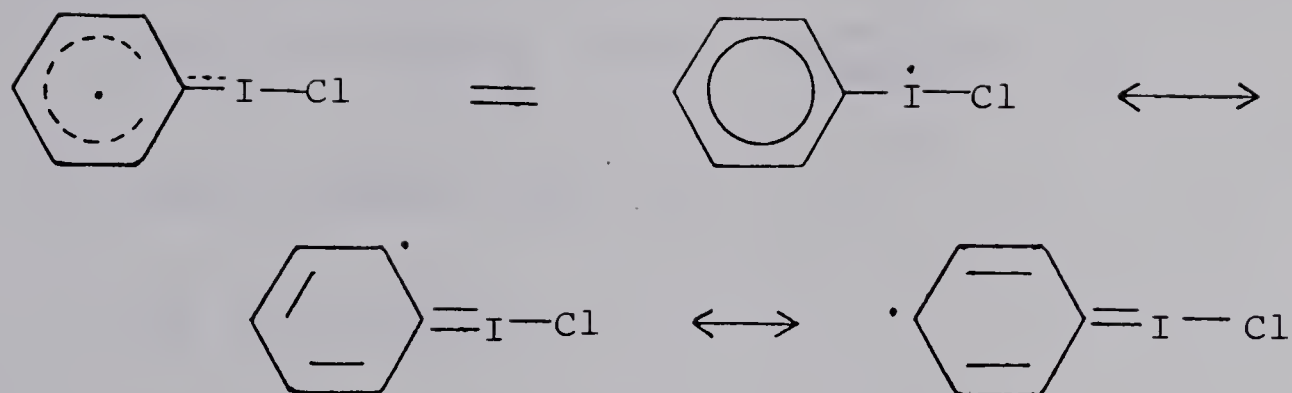


Owing to steric hindrance of reactions at the ortho positions, formation of III is expected to predominate over formation of II for reactions which proceed by Scheme V. Preferential formation of III in a photoinitiated decomposition of IBD contradicts our experimental observations. Therefore, Scheme V can be eliminated as a reaction sequence through which a majority of the rearrangement of IBD occurs. Scheme VI is a radical chain sequence in which the $\text{PhICl}^\bullet$ radical chain transfers with IBD to form intermediate A. Subsequent decomposition of A results in formation of hydrogen chloride and II or III.

SCHEME VI



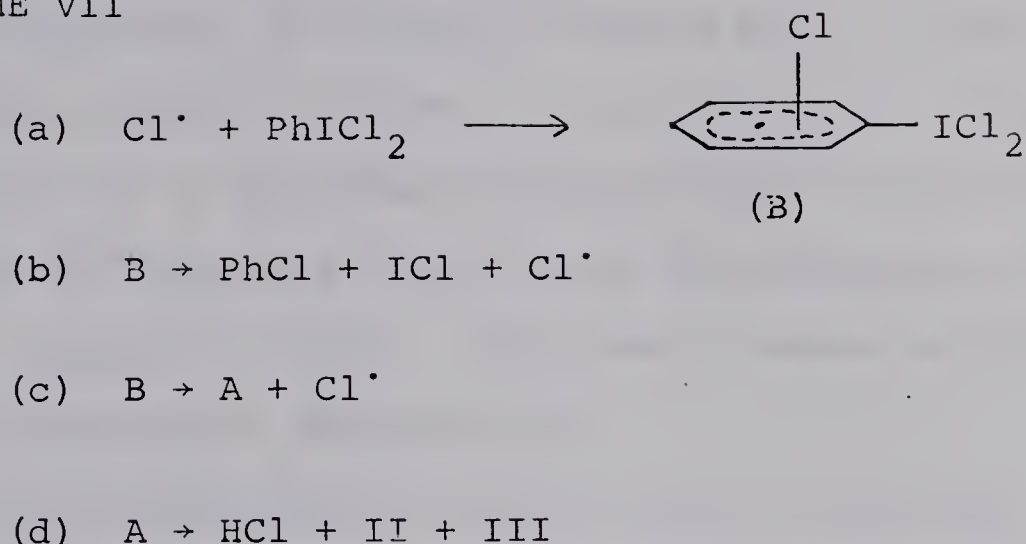
The $\text{PhICl}^\bullet$ radical can exist as a resonance hybrid of the structures shown below. The resonance forms indicate that the free electron of the $\text{PhICl}^\bullet$ radical is localized at the ortho and para positions of the benzene ring as well as at the iodine.



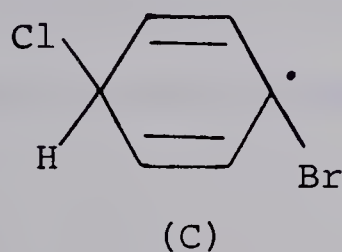
Induction of electrons from the ring by the electronegative chloriodo group opposes the mesomeric delocalization of the free electron toward the phenyl system. The net result of the opposing electronic effects on the PhICl intermediate can conceivably be a phenyl ring which is not greatly deactivated for homolytic reactions and which has electrons localized at the ortho and para positions. Nearly statistical amounts of II and III, i.e. $\text{II/III} = 2$, are expected by ring chlorination of the PhICl radical by chain transfer (VIa) followed by decomposition of the resulting intermediate. Deviations from statistical amounts of II/III can be attributed to steric and polar effects on reactions at the ortho positions.

Reaction scheme VII is a homolytic attack of atomic chlorine on IBD through a pi complex (B). Formation of a pi complex analogous to B has been proposed for displacement of bromine from bromobenzene by atomic chlorine (27, 28).

SCHEME VII



Although displacement of iodine (VIIb) is undoubtedly the primary process subsequent to formation of B, some conversion of B into a sigma complex A also can be expected in accordance with the observation that traces of poly-chlorinated addition products were detected in non-irradiated reactions between molecular chlorine and bromobenzene (27). A sigma complex (C) was proposed as the intermediate leading to formation of the addition products.



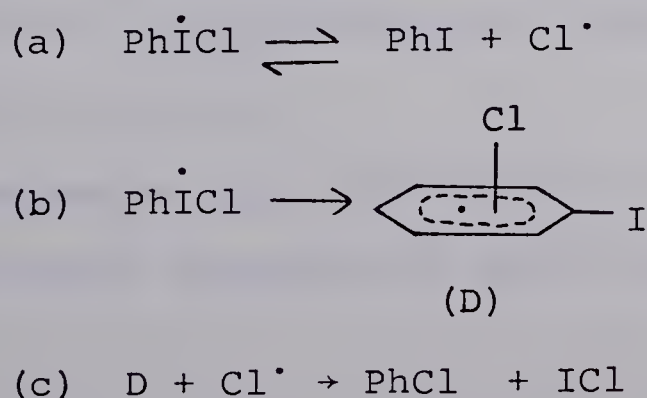
Transformation of B into A can be considered as a process which is analogous to formation of C and is accompanied by concurrent elimination of atomic chlorine. Decomposition of A results in formation of hydrogen chloride and chlorinated iodobenzenes (VIId).

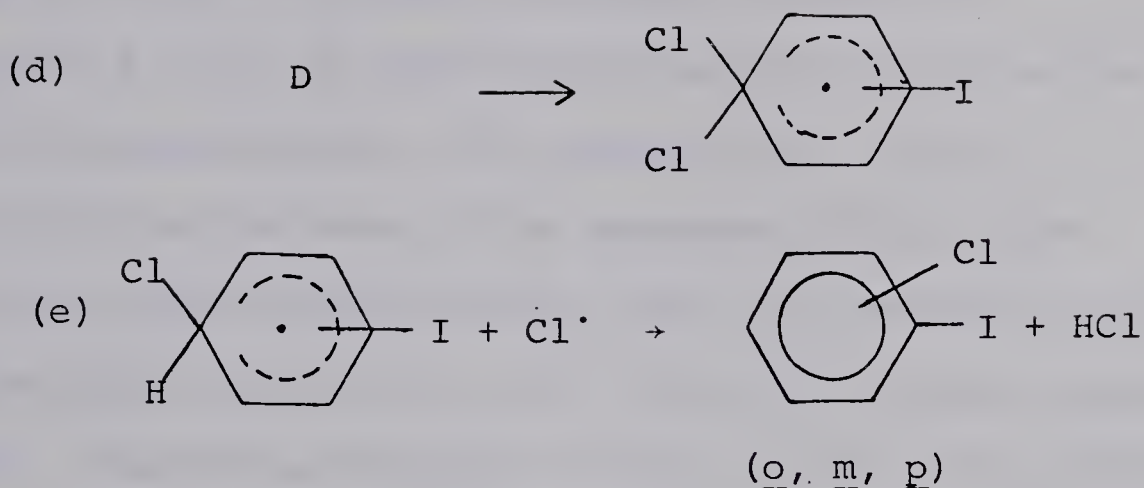
Scheme VII is unlikely to be a major process for two distinct reasons. First of all, formation of the pi complex (B) is an unfavorable process (17) and secondly, Scheme VII predicts formation of chlorobenzene as the major aromatic product. Both requirements contradict our experimental observations.

The intramolecular schemes which have been considered as homolytic sequences for the rearrangement of IBD involve a rearrangement of the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical itself (Scheme VIII) or geminant cage recombination (Scheme IX).

Rearrangement of the $\text{Ph}\dot{\text{I}}\text{Cl}$ radical itself by an internal transfer of atomic chlorine from iodine to the phenyl ring is shown in Scheme VIII. The pi complex (D) formed in that manner can be converted into chlorobenzene by displacement of iodine (VIIIc) or may proceed by a process (VIId,e) which is analogous to that proposed for homolytic aromatic substitution (29) to form hydrogen chloride and isomeric chloriodobenzenes.

SCHEME VIII





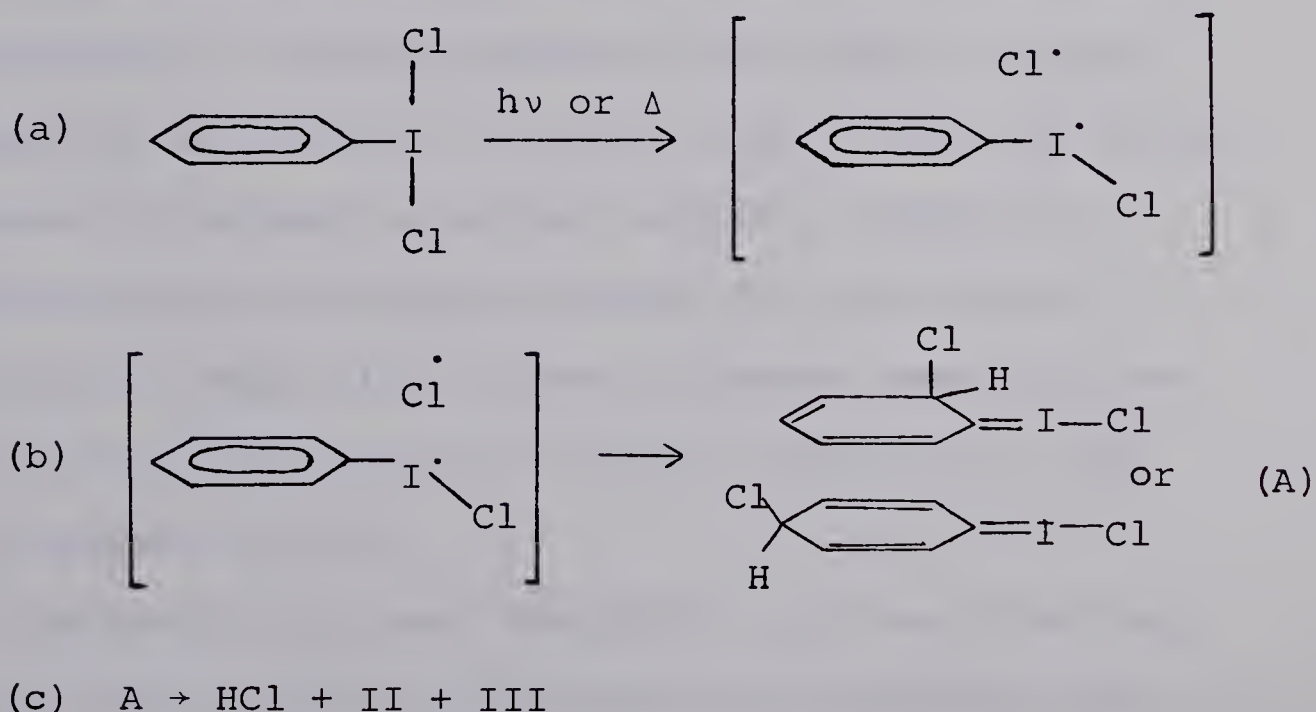
Reaction Scheme VIII can be discounted as a major reaction sequence for two reasons. Firstly, almost exclusive formation of chlorobenzene is expected by displacement of iodine from D. Secondly, the isomeric distribution of chloriodobenzenes formed in sequence VIIId,e is expected to correspond to that observed for vapour phase homolytic halogenation of halobenzenes, i.e. o:m:p $\approx$ 1:6.6:2.5 (30). Neither of the requirements for having Scheme VIII as the main reaction sequence comply with our experimental observations. Nevertheless, Scheme VIII must be considered in order to account for the small amounts of chlorobenzene and the traces of 3-chloriodobenzene which were detected in the reaction products.

Sequence VIIa,b and sequence VIIb,c are the only conceivable processes by which chlorobenzene can be

formed by rearrangement of IBD. Formation of the pi complex (B) between atomic chlorine and IBD is unfavorable owing to deactivation of the phenyl system by the electronegative $-ICl_2$ group (17). The pi complexed intermediate (D) in sequence VII Ib,c also involves a deactivated benzene ring, but the deactivation is expected to be smaller than that of the phenyl system of IBD. Therefore, sequence VII Ib,c is the more probable route leading to formation of chlorobenzene. Equilibrium VII Ia can be considered as a preliminary step leading to displacement of iodine from iodobenzene in the reaction between iodobenzene and sulfuryl chloride (25).

Reaction Scheme IX depicts cage recombination of atomic chlorine with the $PhICl$ radical.

SCHEME IX



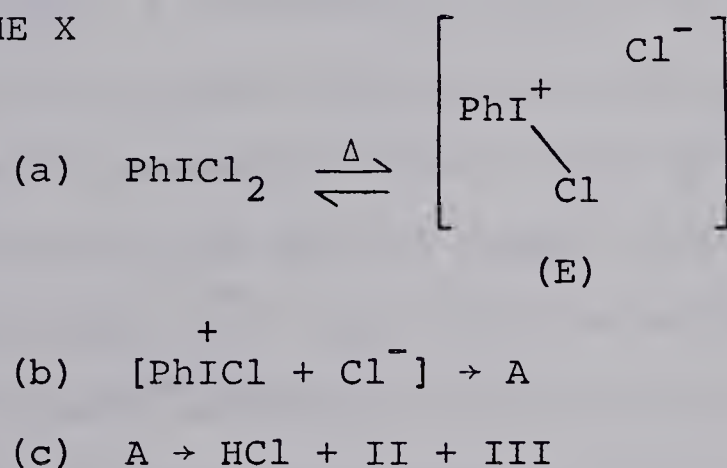
The electronic effects of the $\cdot\text{ICl}$ substituent on the phenyl system of PhICl radicals have been discussed in conjunction with Scheme VI.

Recombination of the unsolvated radicals (IXb) is expected to be subject to less steric hindrance than the chain transfer (VIa) involving solvated intermediates (31). Polar effects are relatively unimportant in electrophilic reactions at the ortho positions on iodobenzene (32) and are expected to be even less important in homolytic reactions. Owing to the proximity of the chlorine atoms of IBD to the ortho carbons of the phenyl ring, cage recombination is expected to result in predominant formation of II. Cage recombination of atomic chlorine and the PhICl radical as depicted in Scheme IX appears to be the most reasonable homolytic sequence that has been considered. Intermolecular chlorine abstraction by PhICl radicals (Scheme VI) and Scheme IX differ only in that the former sequence is subject to solvent effects. Owing to uncertainty of the solvent effects on the chlorine abstraction step (VIa), Scheme VI cannot be discounted as a predominant homolytic reaction sequence for the rearrangement of IBD.

Thermally initiated homolytic reactions involving IBD and reactive substrates have been observed (1,2). Thermally induced dissociation of IBD into iodobenzene and molecular chlorine has also been observed (23), and

is a likely competitive process to thermally induced homolysis of IBD into atomic chlorine and PhICl radicals. The dissociation is believed to proceed through a polarized intermediate (E) in which negative polarization is directed toward the chlorine atoms. Scheme X depicts a reaction sequence in which formation intermediate A occurs by a nucleophilic attack of the Cl^- chloride ion upon the phenylchloroiodinyl cation (PhICl^+).

SCHEME X



Recombination by step Xb is expected to yield products which are chlorinated at the ortho and para positions to the initial chloroiodo substituent. Although ortho substitution is statistically favoured, substitution at the para position is expected to predominate owing to steric and deactivating polar effects on reactions at the ortho position.

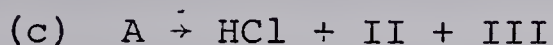
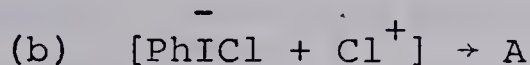
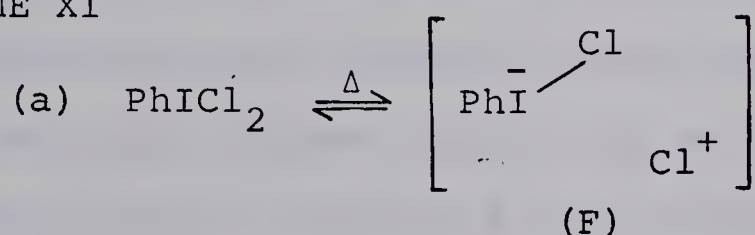
Reactions at the ortho carbons of iodobenzene are relatively unaffected by deactivating polar effects. As a result the distribution of isomeric ring substituted products which is observed is largely due to steric

hindrance of reactions at the ortho positions (32).
 When the substituent is Ph^+ICl , the inductive effect of the substituent is greater than that of $-\text{I}$ owing to the electronegativity of the chlorine and to the electron deficiency within the substituent. As a result of the inductive effect of the Ph^+ICl group the electron density about the ortho carbons will be lower than that about the carbons para to the substituent. Therefore, a nucleophilic attack on the Ph^+ICl is expected to favor reactions at the ortho positions. A competing mesomeric effect which favors the para position as the site of lowest electron density predominates over the inductive effects when the substituent is highly electronegative (32). The net result of the steric, mesomeric, and inductive effects of the phenylchloroiodinyl cation is a phenyl system which is activated to nucleophilic reactions at the ortho and para positions. However, reactions occur at the para position because the steric and mesomeric effects mentioned above are predominant to the inductive effect.

An alternative ionic sequence is postulated in Scheme XI which assumes formation of a chloronium cation and a phenylchloroiodinyl anion (Ph^-ICl) as the initial ionization step. Withdrawal of the electron pair on the Ph^-ICl anion by induction toward the chlorine atom and by mesomerism through the pi orbitals of the phenyl system is expected to stabilize intermediate F sufficiently

to justify formation of the chloronium cation. The net effect of the induction and mesomerism of PhICl is a phenyl system which is activated to electrophilic attack and has electrons localized at the ortho and para positions. Electrophilic ring chlorination of the PhICl anion by cationic chloronium ions results in formation of the intermediate adduct A (XIb). Subsequent decomposition of A results in formation of HCl and II or III.

SCHEME XI



Chlorination of the PhICl anion by the chloronium cation at the ortho positions is favored statistically but deactivation of electrophilic reactions at the ortho positions by polar and steric effects result in preferential reactions at the para position. The relative importance of the mesomeric delocalization of electrons from iodine on the PhICl anion to the para position of the phenyl system is uncertain, but is not expected to be significant owing to the electron

withdrawal by the chlorine of the chloriodo substituent. Therefore, the isomeric distribution of chloriodobenzenes by Scheme XI is expected to be in agreement with that observed for electrophilic substitutions of iodobenzene, i.e. o:p $\approx$ 41:59 (32).

Four of the six reaction sequences that have been considered can reasonably account for a majority of the products that were observed from the decompositions of IBD. Two radical sequences, chain transfer involving the PhICl radical (Scheme VI) and geminant cage recombination (Scheme VIII); and two ionic sequences, Schemes X and XI, appear to be feasible reaction sequences. Since the homolytic sequences predict predominant formation of II with respect to III, and since the ionic sequences predict the reverse, the ratios of II/III observed in the reaction products were used as a measure of the relative amounts of rearrangement occurring by homolytic versus ionic reaction sequences. Owing to the observation of products which apparently arose from secondary reactions of the primary products, limits must be placed on the values reported for the ratios of II/III. Limits can be imposed on the ratio of II/III by assuming that homolytic displacement of iodine from II and III is the only possible source of the isomeric dichlorobenzenes and molecular iodine.

Further limitations can be placed on the values reported for II/III by considering the possible sources of the dichlorinated iodobenzenes.

Either 1,2-dichloro-4-iodobenzene, 2,4-dichloriodobenzene, or 2,5-dichloriodobenzene can correspond to the observed 1,2,4-trisubstituted dichloriodobenzene. Of the three possible isomers, 2,5-dichloriodobenzene and 1,2-dichloro-4-iodobenzene should be preferentially formed by ionic chlorination of chloriodobenzene in compliance with the directive effects of halogen substituents on further halogenations of halobenzenes (33). The 2,5-isomer possibly can be formed by chlorination of either 2-chloriodobenzene or 3-chloriodobenzene; and 1,2-dichloro-4-iodobenzene can arise from subsequent chlorination of either 4-chloriodobenzene or 3-chloriodobenzene. Chlorination of only 2-chloriodobenzene can result in formation of 2,3-dichloriodobenzene or 2,6-dichloriodobenzene.

The ratios of II/III can be recalculated with allowances for all of the various possible sources of secondary products. The ratios of II/III obtained in that manner, however, are presumptuous owing to uncertainties in identification and in quantitative analysis of the dichlorinated iodobenzenes. Nevertheless, mean values for the "corrected" ratios of II/III are

reported in Table XV. The upper and lower limits which were observed in the recalculated values are included in Table XV. Although overlapping occurred between the upper and lower limits of the ratios of II/III, the mean values observed confirmed the distinction between the ratios of II/III observed for irradiated as opposed to those from non-irradiated decompositions of IBD.

Further conclusions can be made regarding the maximum quantity of 3-chloriodobenzene formed in decompositions of IBD by considering the amounts of dichlorinated iodobenzenes that were formed. Assuming that the entire amount of dichlorinated iodobenzene was derived from chlorination of 3-chloriodobenzene, the maximum yield of 3-chloriodobenzene is 0.1 mole/mole IBD and the ratios of o:m:p are approximately 1:0.4:0.7-1.4. Since the isomeric distribution from a homolytic halogenation of a halobenzene is expected to resemble o:m:p $\approx$ 1:6.6:2.5 (30), ring chlorination of IBD or iodobenzene by normal homolytic aromatic substitution can definitely be discarded as principal reaction mechanisms.

Reaction of IBD with substrates are inhibited by free-radical inhibitors (1), but the photoinitiated rearrangement of IBD is not susceptible to experimentally significant inhibition. The lack of inhibition indicates

TABLE XV

CORRECTED RATIOS OF 2-CHLOROIODOBENZENE/4-CHLOROIODOBENZENE
IN PRODUCTS FROM DECOMPOSITION OF IBD

Reaction Conditions	0°, hν	40°, hν	40°, dark
Solvent	Ratio of 2-Chloriodobenzene/4-Chloriodobenzene		
100% CCl ₄	1.30 ± 0.30 ^a (1.89; 1.04) ^b	1.17 ± 0.17 (1.46; 0.88)	0.69 ± 0.03 (0.71; 0.66)
0.61 M C ₆ H ₅ CH ₃ ^c	1.14 ± 0.08	0.58 ± 0.00	0.53 ± 0.02
0.63 M C ₆ H ₆ ^c	0.79 ± 0.10 (0.96; 0.64)	1.00 ± 0.19 (1.35; 0.62)	0.70 ± 0.17 (1.06; 0.45)
100% C ₆ H ₆	1.20 ± 0.20 (1.40; 1.00)	1.03 ± 0.03	0.77 ± 0.02

^a Errors reported are standard deviations from the calculated mean values.

^b Parenthesized values are the maximum and minimum values obtained for ratios of II/III by applying the correction for secondary reactions.

^c The bulk of the solvent was composed of carbon tetrachloride.

either that the intermolecular homolytic process (Scheme VI) does not occur and the homolytic rearrangement is an intramolecular cage recombination, or that the free-radical intermediates in Scheme VI, $\text{Ph}\dot{\text{I}}\text{Cl}$ and $\text{Cl}\cdot$, are unaffected by the inhibitors employed in this investigation.

Solvent effects were observed in the photoinitiated rearrangement of N-bromoacetanilide when benzene and toluene were included in the solvent (34). The solvent effect which appeared to be proportional to the π complexing ability of the solvent was evident by a reduction in the ratio of 2-/4-bromoacetanilide in the products. A similar solvent effect was anticipated for the photoinitiated rearrangement of IBD if the homolytic sequence involved was an intermolecular process. However, both toluene and benzene are more susceptible to chlorination than any of the possible intermediates involved in the rearrangement of IBD; hence rearrangement became secondary to reaction with solvent. Nevertheless, valuable information was gained from the decompositions of IBD in solvents containing benzene or toluene.

Ring chlorinated toluenes were detected along with the anticipated major product, benzyl chloride, in reactions of IBD with toluene. Yields of benzyl chloride were 1.4 (0°) to 2 (40°) times larger than those of ring chlorinated toluene in the products from irradiated

reactions of IBD with toluene. Conversely, the yields of ring chlorinated toluenes were three times larger than those of benzyl chloride for non-irradiated reactions of IBD with toluene at 40°.

Dissociation of IBD is negligible at low temperatures in solvents of low polarity (23). Photolysis initiates a chain reaction between $\text{Ph}\dot{\text{I}}\text{Cl}$ radicals and toluene which results in formation of benzyl chloride (2). Immeasurable traces of chlorobenzene and iodine were detected in the products of reactions between IBD and toluene; thus indicating that a displacement of iodine had occurred. Iodine monochloride (ICl) can be formed either as a product of the displacement reaction VIIIC or by a reaction of molecular chlorine and molecular iodine. Since ICl effectively catalyses non-irradiated chlorination of toluene in solvents of low polarity (24), the apparently anomalous ring chlorination of toluene can be accounted for.

The ratios of II/III observed in the products from irradiated and non-irradiated reactions of IBD with toluene at 40° were approximately equal to that observed in the products from thermally induced, non-irradiated rearrangements of IBD in carbon tetrachloride (See Table XV, p. 71). The anomalously small ratio of II/III in the products from irradiated reactions at

40° can be attributed to a chain reaction of the available PhICl radicals with toluene, thereby leaving rearrangement of IBD to proceed exclusively by an ionic reaction scheme. Although the ratio of II/III observed in the products from photoinitiated reactions between IBD and toluene at low temperature (0°) was depressed from that observed in the absence of toluene, the value observed was within experimental error of the ratio of II/III for irradiated decompositions of IBD in carbon tetrachloride (see Table XV, p. 71). Therefore, some homolytic rearrangement of IBD occurs in photoinitiated reactions at low temperatures, apparently by the intramolecular cage recombination sequence (Scheme VIII).

In solvents containing benzene, the only apparent reaction competing with rearrangement of IBD is the ionic chlorination of benzene. No addition products from radical chlorination of benzene were detected and the yields of hydrogen chloride were approximately equal to those detected in rearrangements of IBD in carbon tetrachloride. The failure to observe radical addition products in the photoinitiated decompositions of IBD in benzene substantiates the proposal that rearrangement of IBD is a cage recombination reaction.

The products from decompositions of IBD under all reaction conditions in 0.63 M benzene contains nearly

equal mixtures of chlorobenzene and the usual IBD rearrangement products. Unlike toluene, benzene apparently can solvate PhICl radicals or atomic chlorine without participating in a free-radical reaction with the intermediates which competes with homolytic rearrangement of IBD. Therefore, the large depression in the ratio of II/III in the products from photoinitiated decompositions of IBD in 0.63M benzene at 0° (see Table XV, p. 71) can be attributed to steric hindrance upon reactions of the solvated intermediates at the ortho positions (31). An alternative explanation for the decrease in the ratio of II/III is that the presence of benzene causes all reactions of IBD, rearrangement and chlorination of benzene, to take place exclusively by ionic mechanisms.

The results of rearrangements of IBD that were carried out in neat benzene at elevated temperatures support the theory that benzene induced an entirely ionic reaction to occur. Ionic reactions are more favorable in benzene than in carbon tetrachloride owing to the greater polarity of benzene. Chlorobenzene was formed, almost exclusively, as the chlorinated organic product of reactions between IBD and neat benzene at 40° . Iodobenzene was formed quantitatively; but yields of hydrogen chloride and material balances for chlorine were somewhat below quantitative. The ionic chlorination

of benzene is by far the predominant reaction, but free-radical addition of chlorine to benzene cannot be discounted as a minor side reaction for reactions of IBD and neat benzene at elevated temperatures.

Although a large reduction in the ratio of II/III was observed in irradiated reactions of IBD in 0.63 M benzene at 0°, the ratios of II/III observed at elevated temperatures in either dilute or neat benzene were unchanged from values observed in carbon tetrachloride. Similarly, the ratio of II/III in the products from photoinitiated decompositions of IBD in neat benzene at 0° was unaltered from that observed for irradiated decompositions of IBD in carbon tetrachloride at 0° (see Table XV, p. 71). Larger yields of chlorinated iodobenzene were detected in the products from irradiated decompositions of IBD in neat benzene at 0° than were observed in either irradiated or non-irradiated decompositions of IBD in neat benzene at 40°. The foregoing results further substantiate the occurrence of homolytic rearrangement of IBD by an intramolecular reaction sequence.

None of the individual reaction sequences proposed will unequivocally account for the distribution of products observed in the decompositions of IBD. The decomposition proceeds by concurrent ionic and free-radical mechanisms. The homolytic mechanism

is predominant in photoinitiated reactions at low temperature and the ionic mechanism predominates in non-irradiated reactions.

Concluding from the evidence obtained in this investigation, geminant cage recombination (Scheme IX) is the predominant homolytic reaction sequence involved in the rearrangement of IBD itself. A small portion of the homolytic reaction must proceed by rearrangement of the $\text{PhICl}^\bullet$ radical itself to account for formation of chlorobenzene (Scheme VIIIa, b, c).

No experimental evidence is available to indicate which of the two ionic sequences is predominant in the rearrangement. Intuitively one would expect that the ionic mechanism involved in the rearrangement has a common intermediate with the ionic reactions of IBD with substrates.

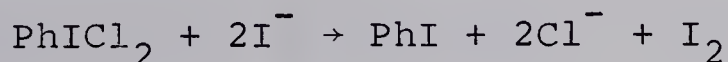
The rate of ionic chlorination of aromatic substrates when IBD is used as the chlorinating reagent is equal to the rate of dissociation of IBD, but molecular chlorine is believed to be the actual chlorinating agent (23). If formation of the polarized intermediates E or F is the rate determining step for dissociation of IBD, identical kinetics would be observed for halogenation of the substrates by the polarized intermediate (F) and for halogenation by a mechanism in which slow dissociation of IBD preceded

a rapid chlorination of substrate by molecular chlorine. However, molecular chlorine does not ionically chlorinate toluene or benzene at an appreciable rate in non-polar solvents unless a Friedel-Crafts catalyst is present. Since electrophilic chlorinations of aromatic substrates require chloronium ions or positively polarized chlorine, reactions of intermediate (F) with the aromatic compounds may be feasible. Alternatively, a transfer of chloronium ions from the PhICl^+ ion to the aromatic substrate also may be feasible. The evidence available from this investigation is insufficient to enable a distinction to be made between the two ionic mechanisms, Scheme X and Scheme XI, which were proposed for the rearrangement of IBD.

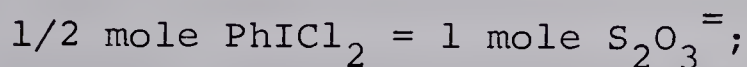
EXPERIMENTAL

Materials

Iodobenzene dichloride was prepared by the reaction of molecular chlorine and iodobenzene in anhydrous chloroform (35). Crude material was recrystallized from a solution of chloroform and petroleum ether (bp 60-70°), washed with petroleum ether (bp 60-70°), and air dried immediately prior to use. The purity of the IBD used was determined by iodometric titration (36) employing the following stoichiometric relationships:



From the stoichiometry it is evident that



therefore the percent purity can be expressed as follows:

$$\% \text{purity} = \frac{\text{ml S}_2\text{O}_3^{=} \times \text{mol wt IBD} \times M \text{ S}_2\text{O}_3^{=}}{2 \times \text{mg IBD}} \times 100$$

The IBD used in all experiments was 97-100% pure as determined by the foregoing analytical method.

Commercial carbon tetrachloride, benzene, toluene, chlorobenzene, Freon 112, and Freon 113 were distilled from phosphorous pentoxide before use.

Chlorobenzene, o-dichlorobenzene, p-dichlorobenzene, iodobenzene, 2-chloriodobenzene, 3-chloriodobenzene, 4-chloriodobenzene, 1,2-dichloro-4-iodobenzene, 2-chlorotoluene, 4-chlorotoluene, and benzyl chloride were used as reagent grade materials, without further purification, for peak enhancement experiments. The same compounds were purified by preparative glpc before use as authentic materials for infrared analysis on a Perkin-Elmer Model 421 Recording Spectrophotometer.

Reagent grade sym-trinitrobenzene, p-hydroquinone, and 2,6-di-t-butyl-4-cresol were used as inhibitors without further purification.

Synthesis of Ring Dichlorinated Iodobenzenes

The procedure used for preparation of 2,3- , 2,4- , 2,5- , 2,6- , and 3,5-dichloriodobenzene from commercially available dichlorinated anilines was a variation of the Sandmeyer reaction in which the diazonium salt was reacted with potassium iodide according to the method of Ullman (37). Small amounts of the crude products were purified by preparative glpc using a 10' x 1/4", 10% SE-30 on 60/80 mesh chromasorb W column in an Aerograph Model 202 Gas Chromatograph. Samples of purified products were submitted for infrared analysis on a Perkin-Elmer Model 421 Recording Spectrophotometer and molecular weight determination by mass spectrometry on

an Associated Electronics Limited MS-9 Mass Spectrometer. The mass spectra of the collected products all had fragmentation patterns that were consistent for ring dichlorinated iodobenzenes. The m/e observed for the parent ions were invariant from m/e (271.8659) for a compound with a molecular formula of $C_6H_3Cl_2I$. The infrared spectra will be discussed below in conjunction with the identification of the products from decompositions of IBD.

2,3-Dichloriodobenzene - The purified product was a pale yellow solid that melted at $34-35^\circ$ * [lit. (38) mp 36°] and for which the observed m/e was 271.8659.

2,4-Dichloriodobenzene - A clear colorless liquid was collected as purified material, bp 260° [lit. (39) $262-263^\circ$]; m/e 271.8659.

2,5-Dichloriodobenzene - A clear colorless liquid, bp 249° [lit. (38) bp $250-251$] was collected. The liquid solidified upon cooling to form a white solid, mp 21° [lit. (40) mp 21°]; m/e 271.8660.

2,6-Dichloriodobenzene - A white solid was collected which has a melting point of $63-64^\circ$ [lit. (41) mp 68°]; m/e 271.8657,

* All reported temperatures are uncorrected.

3,5-Dichloriodobenzene - White spars, mp 54°
[lit. (42) mp 54°]; m/e 271.8658, were obtained from recrystallization of the crude 3,5-dichloriodobenzene from 95% ethanol.

The isomeric dichlorinated iodobenzenes were not resolvable by thin layer chromatography on 3" and 8" plates coated with either silica-gel GF or alumina GF when either petroleum ether (bp 60-70°) or carbon tetrachloride were used as eluants.

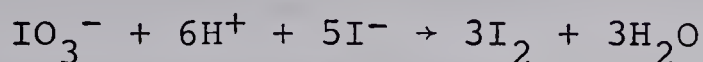
General Method of Reaction

Reactions were carried out in sealed Pyrex ampules. All glassware was washed with chromic acid, soaked in dilute ammonium hydroxide, rinsed thoroughly with distilled water, and dried in an oven at 110° before use.

Solvent solutions which contained 0.32 M Freon 112 or 0.145-0.290 M Freon 113 as internal reference standards were prepared in 25 or 50 ml volumetric flasks.

Solvents containing hydrogen chloride were prepared by bubbling gaseous hydrogen chloride, which had been dried by passing over calcium chloride, through ice chilled solvents which were freshly distilled from phosphorous pentoxide. The solutions were then diluted to the desired concentrations by addition of anhydrous solvent. The concentration of hydrogen chloride was

determined by iodometric titration (43) before use, and re-examined after all of the reaction vessels had been prepared. In all cases, the hydrogen chloride concentration remained constant. The following stoichiometric relationships were used for hydrogen chloride determinations:



Therefore:

$$M \text{ HCl} = \frac{M \text{ S}_2\text{O}_3^{2-} \times \text{ml S}_2\text{O}_3^{2-}}{\text{vol HCl solution in CCl}_4 \text{ (ml)}}$$

Reaction mixtures were prepared in diffuse light by the following general procedure. Dry, freshly recrystallized IBD was weighed (0.3-0.5 g) into Pyrex reaction vessels which had been wrapped in foil. Appropriate amounts of solvent mixtures (3-5 ml) were accurately pipetted into the ampules in order to maintain a 0.1 g per ml solute to solvent ratio. The vessels were sealed after being degassed twice by the freeze-thaw method.

Vessels containing materials for reactions to be carried out in the presence of atmospheric amounts of oxygen were stoppered tightly before their contents were frozen in liquid nitrogen; thereupon they were

sealed as before, but without degassing.

The foil-wrapped ampules were allowed to equilibrate in baths of appropriate temperature before being irradiated by two Hanovia, Model 30620, medium-pressure mercury vapor ultraviolet lamps; or by several (2-4) 200 watt incandescent bulbs. Vessels containing mixtures for decompositions in darkness were left wrapped in foil in the thermostated baths.

Decompositions at 40° were carried out in a water bath thermostated at $40 \pm 0.2^\circ$; at 75° in an oil bath thermostated at $75 \pm 0.5^\circ$; and at 0° in an ice-water mixture or in a Colera Low Temperature Thermostat Bath, Type KT 40 S. Reactions carried out at 0° in ice-water mixtures were agitated constantly throughout irradiation periods. All vessels were wrapped in foil and stored at -10° whenever irradiation was interrupted.

The Colera bath contained a 35% ethylene glycol-water solution which was thermostated at $0 \pm 0.2^\circ$. No constant shaking of reaction vessels was possible when the mechanical cooler was employed, and only one ultraviolet lamp could be used for irradiation of the samples. As a result, decompositions in the mechanical cooler required 2-3 times longer than for those thermostated in ice-water mixtures.

Ampules containing IBD for decompositions in darkness at 0° were wrapped in foil and stored in a refrigerator. The vessels were shaken occasionally during the reaction period.

Reactions were allowed to proceed until the heterogeneous mixtures of yellow solid in a pale yellow solution (carbon tetrachloride solvent) or yellow solution (benzene solvent) transformed into a dark amber (carbon tetrachloride) or violet (benzene) solution. Upon completion of reactions, the vessels containing final reaction mixtures were wrapped in foil and stored at -10° to await analysis.

For analysis, the contents of a reaction vessel were frozen in liquid nitrogen and the ampule was opened. Its contents were transferred immediately into a glass stoppered 250 ml Erlenmeyer flask containing about 100 ml of distilled water. The stopper was held tightly in place to minimize escape of hydrogen chloride while the mixture in the Erlenmeyer flask was stirred in order to promote solution of the hydrogen chloride.

Following iodometric titration for unreacted chlorine (as well as free iodine) and hydrogen chloride with 0.1 M sodium thiosulfate, the organic portion of the resulting mixture was extracted and analysed by glpc.

Isolation and Identification of Reaction Products.

Products were identified by comparison of their retention times with those of authentic materials on several different glpc columns which are listed below:
10' x 1/8", 5% SF-96 on 80/100 mesh chromasorb W/AW;
10' x 1/8", 5% SE-30 on 80/100 mesh firebrick;
10' x 1/8", 5% Carbowax on 80/100 mesh chromosorb W on an Aerograph Model 1520 Gas Chromatograph; as well as
10' x 1/4", 10% SE-30 on 60/80 mesh firebrick;
and 10' x 1/4", 15% Neopentyl Glycol Succinate (NPGS) on 60/80 mesh chromasorb W/AW on an Aerograph Model 202 Gas Chromatograph.

Individual products were isolated from concentrated reaction mixtures from photoinitiated decomposition of IBD at 0° by preparative glpc using 10' x 1/4", 10% SE-30 on 60/80 mesh chromasorb W/AW columns in an Aerograph Model 202 Gas Chromatograph. Products isolated in that manner were subitted for infrared analysis and for molecular weight determinations by mass spectrometry.

Mass spectra of the collected products were taken on an Associated Electronics Ltd. MS-9 Mass Spectrometer using an ionizing voltage of 70 eV.

The m/e values observed for the parent ions of the collected products are listed in Table XVI in the order of product elution from the gas chromatograph.

TABLE XVI

MOLECULAR WEIGHTS OF PRODUCTS FROM DECOMPOSITION OF IBD ^a

m/e Observed	m/e Calculated	Molecular Formula
112.0081	112.0079	C ₆ H ₅ Cl
145.9688	145.9690	C ₆ H ₄ Cl ₂
203.9432	203.9425	C ₆ H ₅ I
237.9048	237.9036	C ₆ H ₄ ClI
237.9046	237.9036	C ₆ H ₄ ClI
271.8662	271.8647	C ₆ H ₃ Cl ₂ I

^a Products were isolated from reaction mixtures of irradiated decompositions of IBD at 0° in degassed ampules containing carbon tetrachloride as solvent.

Fragmentation patterns observed in the mass spectra of the collected products were consistent with those observed in spectra of corresponding purified authentic materials.

Infrared spectra of the collected products were taken on a Perkin-Elmer Model 421 Recording Spectrophotometer. Spectro grade carbon disulfide was used as a solvent and 0.5 mm potassium bromide cells were employed. The spectra of the collected products were compared with spectra of purified authentic materials as a means of identification.

The infrared spectrum of chlorobenzene which had been collected was identical with that of pure commercial chlorobenzene.

The spectra of other collected products were consistent with spectra obtained from authentic materials. However, due to incomplete resolution of some components, the infrared spectra of collected products contained additional absorption bands which were attributable to strong absorptions in the spectra of adjacent eluants.

Collected p-dichlorobenzene gave a spectrum which had one additional strong absorption at $730\text{--}720\text{ cm}^{-1}$, plus four additional strong absorptions at 1052, 990, 680, and 650 cm^{-1} indicating contamination by iodobenzene.

Three additional peaks (1125 , 1032, and 813 cm^{-1}) were found in the spectrum of collected iodobenzene. Absorption at 1084 and 744 cm^{-1} were proportionately larger in the infrared spectrum of collected iodobenzene than in that of commercial iodobenzene. Enlargement of the absorption at 1084 cm^{-1} and appearance of the additional peak at 813 cm^{-1} can be attributed to p-dichlorobenzene in the collected iodobenzene. Appearance of the other additional peaks at 1125 and 1032 cm^{-1} and enlargement of the peak at 744 cm^{-1} indicated that o-dichlorobenzene was present in the collected sample of iodobenzene.

The spectrum of 2-chloriodobenzene had three more absorption bands than pure, commercial 2-chloriodobenzene. Bands at 1083, 1047, and 803 cm^{-1} corresponded to main absorptions for 4-chloriodobenzene which quite possibly was a contaminant owing to the difficulty encountered in effecting a complete separation of the ortho and para isomers of chloriodobenzene.

4-Chloriodobenzene that had been collected by preparative glpc from a 10' x 1/4", 15% NPGS column (which completely resolved 2-chloriodobenzene and 4-chloriodobenzene) gave an infrared spectrum with four additional absorbances at 861, 763, 733, and 633 cm^{-1} . The additional absorbances corresponded to strong bands

in the infrared spectrum of 3-chloriodobenzene and, therefore, indicated contamination by that isomer.

Infrared spectra of collected material having a m/e of 272, corresponding to a molecular formula of $C_6H_3Cl_2I$, had absorptions characteristic of 1,2,4-trisubstituted benzene (strong absorptions at 1355, 1240, 1140, 1115, 860, and 800 cm^{-1}). The collected material, however, appeared to be a mixture of several components. Strong absorptions at 1357, 1241, 1138, 1116, 862 and 803 cm^{-1} were common in the infrared spectra of the collected material; 1,2-dichloro-4-iodobenzene; 2,4-dichloriodobenzene; and 2,5-dichloriodobenzene. Strong absorptions at 1092 and 1007 cm^{-1} observed in the infrared of the mixture were common strong bands in the infrared spectra of 2,4-dichloriodobenzene and 2,5-dichloriodobenzene. Absorptions at 1060 and 744 cm^{-1} were observed as peaks of medium strength in the infrared spectrum of the collected product as well as in those of 1,2-dichloro-4-iodobenzene and 2,5-dichloriodobenzene. Strong peaks characterizing only 2,5-dichloriodobenzene appeared at 1103 and 1015 cm^{-1} . Peaks for only 2,4-dichloriodobenzene were observed at 1085 and 796 cm^{-1} . Peaks of medium intensity which appeared at 1129, 1026, and 666 cm^{-1} in the spectrum of the collected product, corresponded to major absorption regions in the spectrum of 1,2-dichloro-4-iodobenzene.

Quantitative Analysis of IBD Rearrangement Products

Quantitative glpc analysis of reaction mixtures were carried out on an Aerograph Model 202 Gas Chromatograph using 10' x 1/4", 10% SE-30 on 60/80 mesh firebrick or 10' x 1/4", 15% Neopentyl Glycol Succinate (NPGS) on 60/80 mesh chromasorb W/AW columns. Although the latter columns effected complete resolution of 2-chloriodobenzene and 4-chloriodobenzene, the results of quantitative analysis using NPGS columns were identical with those obtained when SE-30 columns were employed.

The glpc traces were recorded on a Honeywell, ElectroniK 15 Strip Chart Chromatography Recorder. Peak areas were calculated by multiplication of the height by the width at half-height. All analyses were carried out in triplicate and were in agreement to $\pm 4\%$. A typical trace from a glpc analysis is shown in Figure 1.

Area ratios of product/internal standard (Freon 112 or Freon 113) were converted into mole ratios of product/internal standard by referring to calibration curves of area ratios versus mole ratios. The calibration curves were obtained by plotting the area ratios of product/standard as observed by glpc analysis of various synthetically prepared solutions of known concentration. The calibrations were carried out on an Aerograph Model 202 Gas Chromatograph using 10' x 1/4", 10% SE-30 on

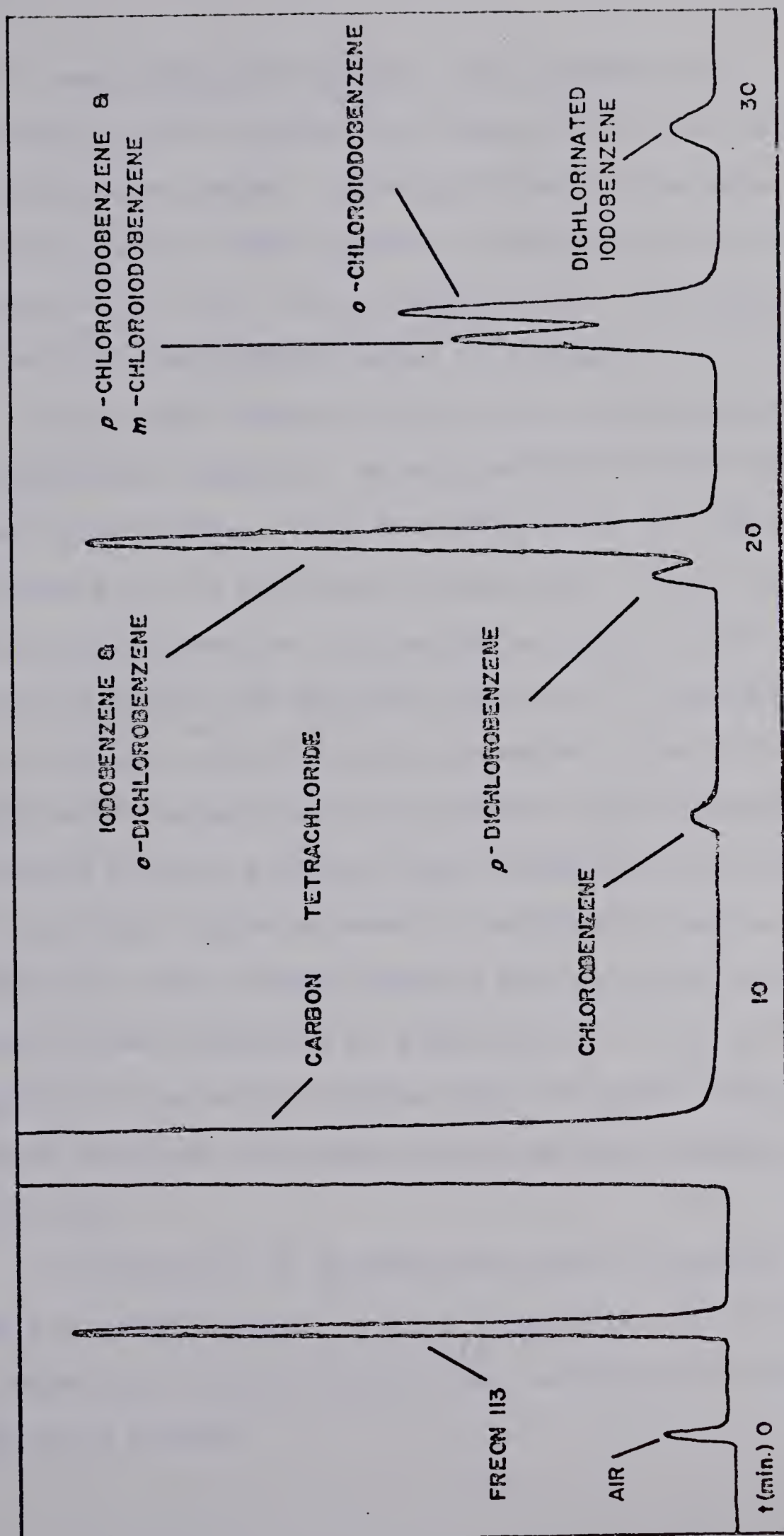


FIGURE 1

TYPICAL G.L.P.C. CHROMATOGRAM (10'x1/4", 10% SE-30) OF PRODUCTS FROM IED DECOMPOSITIONS AT 0° WITH hv

60/80 mesh firebrick columns. All calibrations obtained in this manner were linear in the pertinent concentration ranges. Multiplication of the mole ratios by the moles of Freon present in the reaction mixtures converted the mole ratios observed into the reported values for the absolute moles of products.

Iodine was visible in the final reaction mixtures, but satisfactory iodometric determinations for free iodine alone were unattainable. Only the total titer for iodine plus unreacted active chlorine was observed. Since the lone conceivable route for liberation of iodine under the reaction conditions employed resulted in formation of chlorobenzene and the dichlorobenzenes, one-half of the total molar amounts of chlorobenzene and dichlorobenzene detected by glpc analysis were assigned as the quantity of molecular iodine present in the final reaction mixtures. Thereafter, the values reported for unreacted active chlorine were obtained by subtraction of the calculated quantity of molecular iodine from the gross amount of active chlorine and iodine which had been determined by titration.

The percents of decomposition were determined from the titrimetric data. A titer, equivalent to the amount of unreacted active chlorine, was calculated by the following method:

$$\frac{2 \times \text{Unreacted Active Chlorine (mmole)}}{[\text{S}_2\text{O}_3^{=}] \text{ (M)}} = \text{Titer (ml)}$$

The final titer obtained in that manner was substituted into the expression below:

$$\frac{\text{Initial Titer} - \text{Final Titer}}{\text{Initial Titer}} \times 100 = \text{Percent Decomposition}$$

Initial titers were calculated from the weight and purity of IBD initially present in reaction vessels by substitution into the following equation:

$$\frac{2 \times \text{Purity (\%)} \times \text{Initial IBD (mmole)}}{[\text{S}_2\text{O}_3^{=}] \text{ (M)}} = \text{Titer (ml)}$$

Quantitative Determination of 3-Chloriodobenzene

Examination of the infrared spectra of products isolated from photoinitiated decompositions of IBD at 0° indicated that the product collected as 4-chloriodobenzene was contaminated with less than 10% 3-chloriodobenzene. The spectrum of 3-chloriodobenzene in spectro grade carbon disulfide contained strong absorption maxima at 663, 733, and 763 cm^{-1} , in which region the spectrum of 4-chloriodobenzene was free from major absorbances (compare Figures 2 and 3). Therefore, it was possible to determine the percentage of meta isomer included in the material collected as 4-chloriodobenzene by quantitative

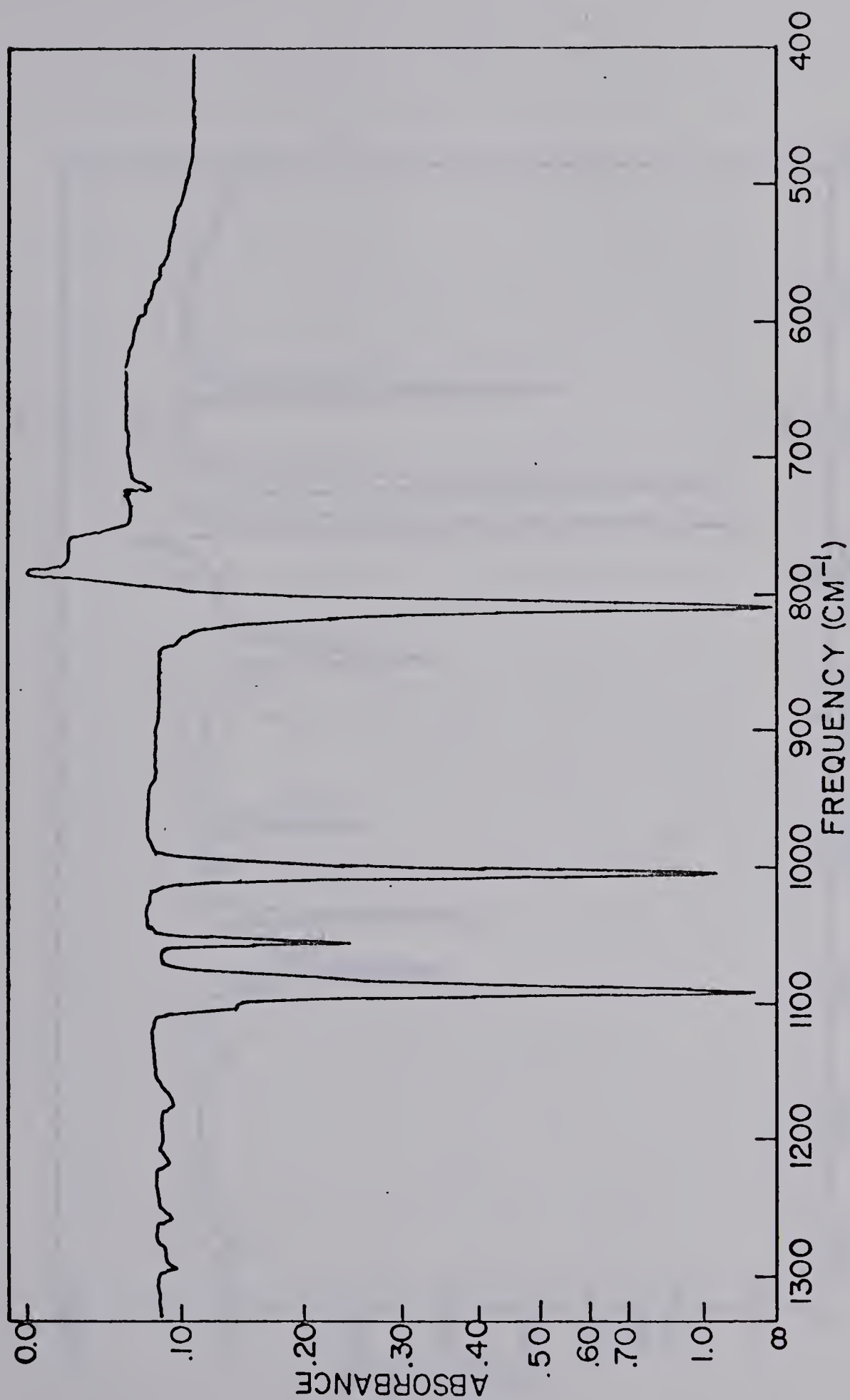


FIGURE 2
p-CHLOROIODOBENZENE
(SOLUTION SPECTRUM IN CARBON DISULFIDE, 0.06M)

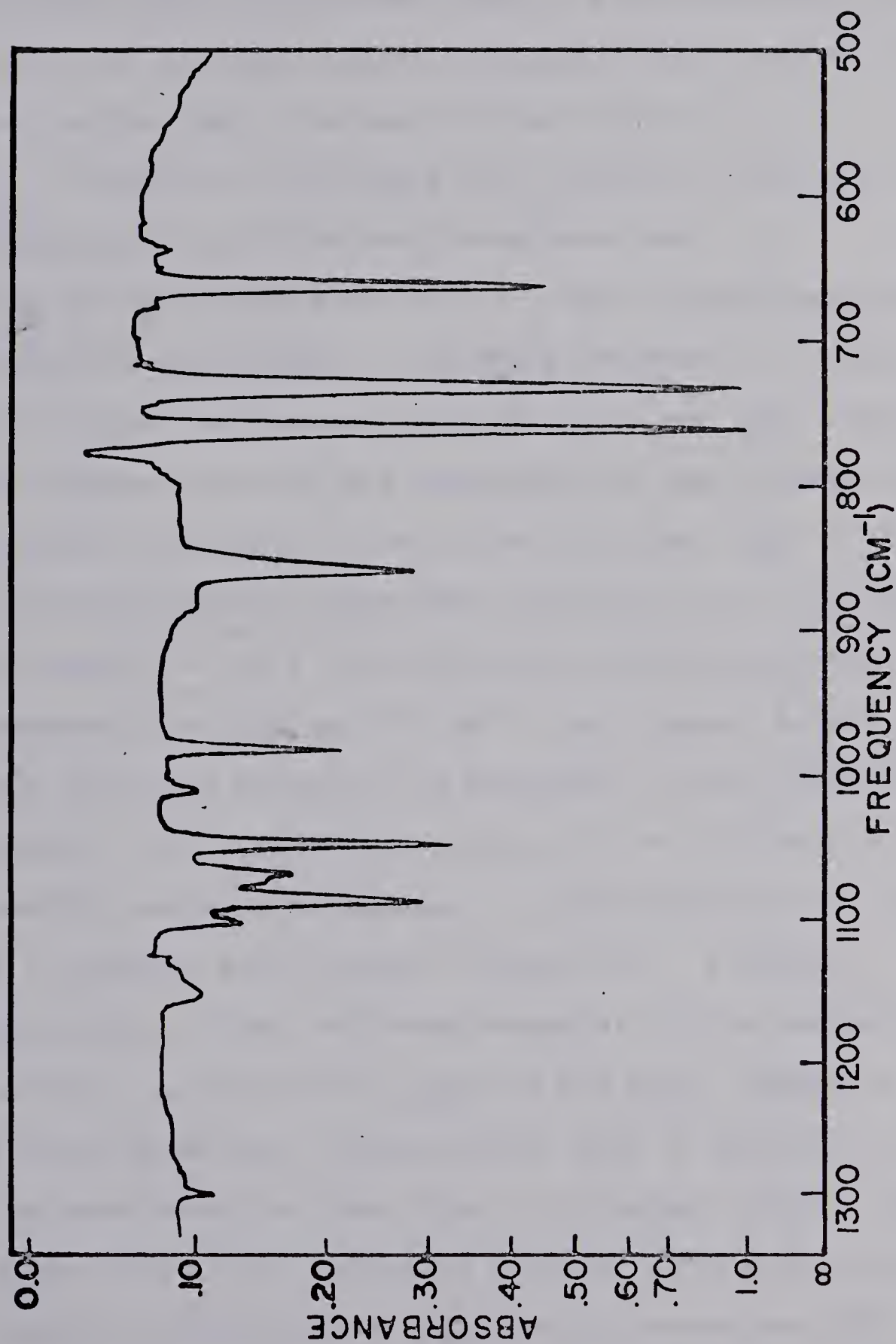


FIGURE 3
m-CHLOROIODOBENZENE
(SOLUTION SPECTRUM IN CARBON DISULFIDE, 0.06M)

differential infrared analysis. A Perkin-Elmer Model 337 Grating Spectrophotometer using 0.5 mm potassium bromide cells was employed for the analyses which were carried out in the region between 400 and 1300 cm^{-1} .

A series of solutions was prepared in which the gross concentration of 3-chloriodobenzene and 4-chloriodobenzene was 0.02 M. Each member contained a different percentage of the meta component. A solution of 4-chloriodobenzene (0.02 M) which had been collected by preparative glpc was compared with the synthetically prepared solutions as described by Tanner (44). The resulting spectra approached linearity (i.e., at constant A , where $A = \log I^0/I$) with slight deviations from constant A at 763 and 733 cm^{-1} (see Figures 4a-c). When the collected material was compared, by the differential method, with a synthetic mixture of 2% 3-chloriodobenzene and 98% 4-chloriodobenzene, an absorbance greater than $A = \text{constant}$ was obtained (Figure 4a). A similar comparison of the collected material with a synthetic solution containing 8% meta and 92% para isomers of chloriodobenzene, respectively, gave a spectrum in which the absorbance was less than $A = \text{constant}$ (Figure 4c). Comparison of the collected material with a synthetic solution containing 6% 3-chloriodobenzene and 94% 4-chloriodobenzene in the same way gave a spectrum with

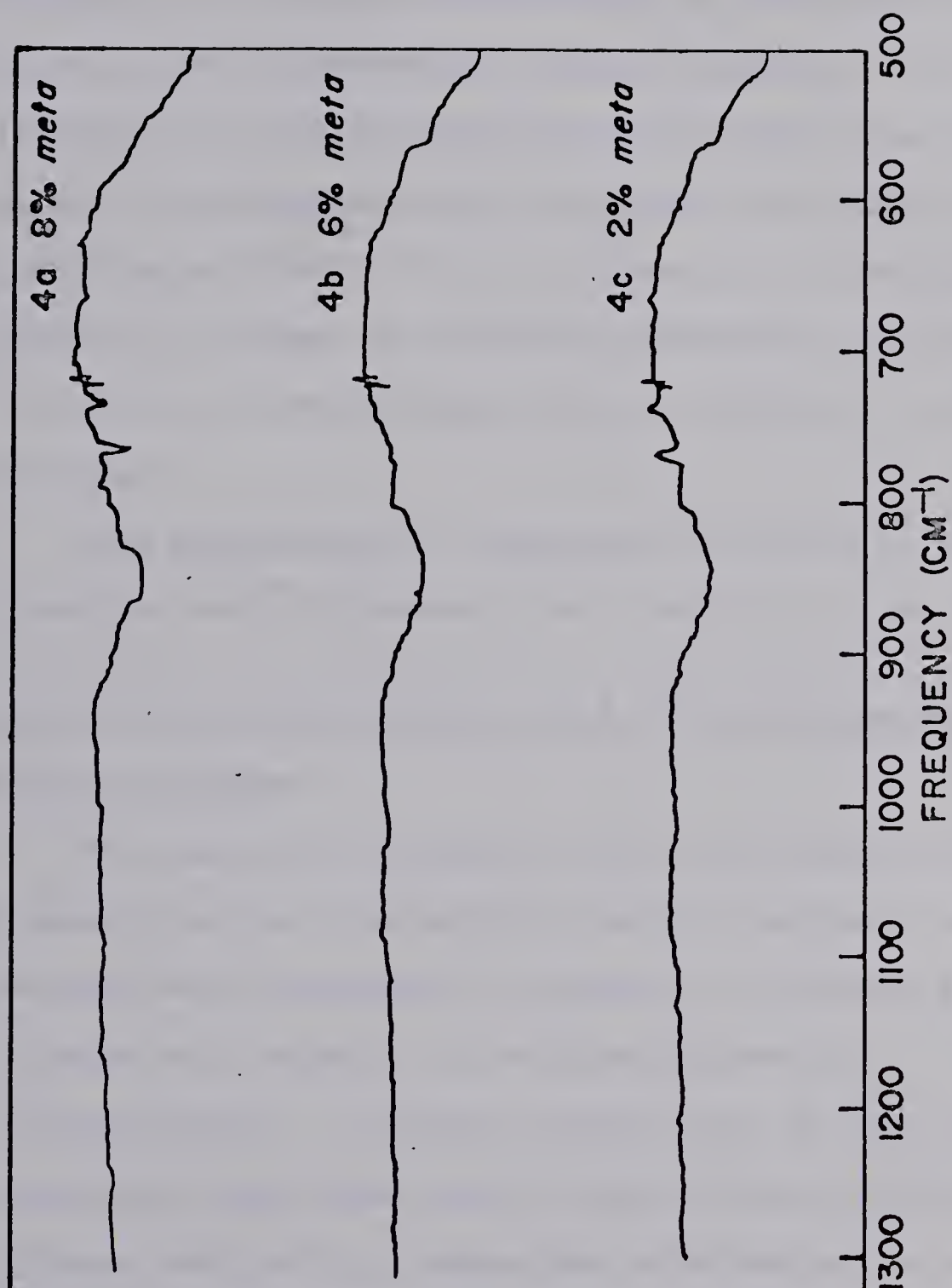


FIGURE 4a,b,c
DIFFERENTIAL ANALYSIS FOR *m*-CHLOROIODOBENZENE
IN PRODUCTS FROM IBD DECOMPOSITION (0°, hv)
(SOLUTION SPECTRA IN CARBON DISULFIDE, (0.02M))

almost no deviation from constant absorbance (Figure 4b).

4-Chloriodobenzene collected from the products of photoinitiated decompositions of IBD at 40° appeared to contain 2% of 3-chloriodobenzene as determined by quantitative differential infrared analysis. The same quantity of 3-chloriodobenzene appeared to be present in the 4-chloriodobenzene isolated from irradiated decompositions of IBD at 0° in the presence of atmospheric amounts of oxygen. No 3-chloriodobenzene was detected in the products from decompositions at either 40 or 75° in darkness.

The percentages of components obtained by the foregoing method apparently are correct to ±3%.

Quantitative Determination of 2-Chlorotoluene and 4-Chlorotoluene

The material isolated as ring chlorinated toluene by preparative glpc analysis of reaction mixtures in which IBD had been decomposed in solvents containing 0.61 M toluene was a mixture of 2-chlorotoluene and 4-chlorotoluene. Relative proportions of the isomeric components were determined by quantitative differential infrared analysis by comparison of absorptions at 746 and 1055 cm^{-1} , which are unique for 2-chlorotoluene, with those at 806 and 1089 cm^{-1} for 4-chlorotoluene. The method employed for analysis of the isomeric chlorotoluenes was

identical to that for analysis of the isomeric chloriodobenzenes. Solutions used in the comparative analyses contained either known mixtures of authentic chlorotoluenes (0.04 M) or collected chlorotoluene (0.04 M) in spectro grade carbon disulfide.

The chlorotoluene collected from the products of either irradiated or non-irradiated reactions at 40° appeared to be 55:45 mixtures of 2-chlorotoluene:4-chlorotoluene. The chlorotoluene collected from the products of irradiated reactions at 0°, however, appeared to consist of a 70:30 mixture of 2-chlorotoluene:4-chlorotoluene.

Quantitative Determination of 1,2-Dichlorobenzene

The infrared spectrum of iodobenzene that had been isolated by preparative glpc from the products of irradiated decompositions of IBD at 0° indicated that o-dichlorobenzene was present in the collected material. Resolution of o-dichlorobenzene and iodobenzene was effected by use of a 10' x 1/8", 5% Carbowax on 80/100 mesh chromasorb W column in an Aerograph Model 1520 Gas Chromatograph. Mole ratios of o-dichlorobenzene/iodobenzene were equivalent to area ratios of o-dichlorobenzene/iodobenzene on the thermal conductivity detector of the Aerograph 1520 Gas Chromatograph that was used for the analysis. A representative reaction mixture

from each set of reaction conditons was concentrated by solvent removal at low temperatures prior to analysis by glpc. Areas of the peaks appearing for o-dichlorobenzene and iodobenzene were determined by multiplication of the peak height by the width at half-height. The mole ratios of o-dichlorobenzene/iodobenzene were determined by comparing the area ratios observed for the respective products. A mole ratio of 0.07 was obtained for the ratio of o-dichlorobenzene/iodobenzene in the products from irradiated decompositions of IBD at 0°. Concentrated reaction mixtures from IBD decompositions at 75° in darkness and 40° with irradiation were analysed similarly. The ratios of o-dichlorobenzene/iodobenzene in the products from the decompositions at 75° and 40° were 0.10 and 0.08 respectively. Owing to the small ratio of o-dichlorobenzene/iodobenzene generally found in the products from decompositions of IBD in degassed reaction vessels having carbon tetrachloride as solvent, the o-dichlorobenzene in products from the remaining reactions in a particular set of reaction conditions was determined by multiplication of the moles of iodobenzene previously found by the ratio of o-dichlorobenzene/iodobenzene found in the representative sample. Then the original quantity of iodobenzene was adjusted accordingly. Neither

o-dichlorobenzene nor p-dichlorobenzene were detected in the products from reactions that were carried out in the presence of toluene. Traces of p-dichlorobenzene were detected, but no o-dichlorobenzene was found in the products from decompositions that were carried out in solvents which contained benzene.

Quantitative Analysis of the Ring Dichlorinated Iodobenzenes

The isomeric composition of the dichlorinated iodobenzenes in the products was equivocal; therefore the quantity of dichlorinated iodobenzene was estimated assuming that a 1:1 ratio existed between the mole ratios and area ratios of the compounds/internal standard. From the precedent established by the linear relationships which existed between mole ratios and area ratios for the other components in the products, a maximum error of $\pm 20\%$ was introduced by employing the assumption. The peak corresponding to dichlorinated iodobenzene on normal analytical glpc chromatograms appeared as one large peak followed by an unresolved, almost immeasurable smaller peak. Figure 1 (p. 92) shows a typical chromatogram with the smaller peak for dichlorinated iodobenzene omitted. Only the larger peak was measurable for quantitative analysis.

Two peaks appeared with retention times corresponding to those of dichlorinated iodobenzene when a concentrated reaction mixture from a decomposition of IBD was analysed on a 10' x 1/8", 5% SE-30 column. The peaks observed were correlated to their components by peak enhancement experiments with purified, synthetically prepared dichlorinated iodobenzenes. One peak which had a retention time equal to those for 2,5-dichloriodobenzene, 2,4-dichloriodobenzene, and 1,2-dichloro-4-iodobenzene was twice the size of the second peak. The latter peak had a retention time equal to those for 2,3-dichloriodobenzene and 2,6-dichloriodobenzene. When synthetically prepared 3,5-dichloriodobenzene was included in an analytical sample of reaction products, neither of the original peaks on the chromatogram which corresponded to the isomers above increased in size. However, a third peak appeared at a retention time approximately equal to those observed for the other dichlorinated iodobenzenes.

Decomposition of Solid IBD

Photoinitiated Decomposition.—Pure IBD (0.2 g; 0.8 mmole) was weighed into a Pyrex ampule which was then degassed and sealed. All of the foregoing operations were carried out in diffuse light. The reaction vessel was kept on ice while being irradiated with a

medium-pressure Hanovia ultraviolet source. The yellow IBD needles transformed into a brown oil after being irradiated for 70 hrs. The contents of the ampule were frozen in liquid nitrogen prior to opening of the vessel. The reaction products were dissolved in about 2 ml of carbon tetrachloride before being titrated with standardized sodium thiosulfate (0.1 M) for unreacted active chlorine, molecular iodine, and hydrogen chloride. Addition of Freon 113 (0.04 mmole) to the organic layer preceded quantitative analysis by the same method as was previously described for reactions in carbon tetrachloride (p. 91). Products were identified by peak enhancement experiments when samples injected into the gas chromatograph contained authentic materials. Molecular weight determination and infrared analysis of collected products verified that the products obtained from decomposition of solid IBD and from decomposition in carbon tetrachloride were qualitatively identical.

Thermally Induced Decomposition - Purified IBD (0.2 g; 0.8 mmole) was weighed into a Pyrex ampule which was then degassed and sealed in darkness. The vessel was wrapped in aluminum foil and placed in an Amberhalter apparatus to be heated by the vapors of refluxing carbon tetrachloride (bp 76° at 690 mm pressure). Within 20 hrs the solid IBD had transformed into a brown oil. The analytical procedure

was identical to that for the photoinitiated decomposition.

Reactions of IBD with Polar Catalysts

Reaction of IBD with ICl - Iodobenzene (0.2 g; 0.1 mmole) and purified IBD (0.27 g; 0.1 mmole) were weighed into a 10 ml Erlenmeyer flask. Approximately 5 ml of carbon tetrachloride was added as a solvent prior to addition of 0.15 g (0.1 mmole) of ICl. The initial reaction mixture consisted of a dark brown solution containing precipitated IBD. The reaction mixture was allowed to stand at room temperature after the stoppered flask had been wrapped in foil. Within 15 minutes the yellow precipitate disappeared, but the solution did not change appearance. Iodometric titration of the final reaction mixture indicated that at least 0.03 mmole of hydrogen chloride was formed in the reaction. Iodobenzene, 2-chloriodobenzene, and 4-chloriodobenzene were detected by glpc analysis using either 10' x 1/4" SE-30 or 10' x 1/4" NPGS columns. Iodobenzene made up 60% of the products that were detected by glpc. The isomeric chloriodobenzenes, in a ratio for II/III of 0.7, made up the remaining products detected in that manner.

Reaction of Iodobenzene with ICl₃ - Iodobenzene (0.4 g; 0.2 mmole) and ICl₃ (0.1 g; 0.04 mmole) were mixed together in a 10 ml Erlenmeyer flask which contained

5 ml of carbon tetrachloride as a solvent. A fine yellow solid precipitated from the amber solution almost immediately after the reagents were mixed together. The flask was stoppered and wrapped in foil, then allowed to stand at room temperature. Within one hour the yellow solid disappeared. At least 0.03 mmole of hydrogen chloride was detected in the final reaction mixture by iodometric titration. Analysis of the final reaction mixture by glpc as above revealed that 2-chloriodobenzene and 4-chloriodobenzene were formed. The ratio of II/III was 0.7.

Reaction of Iodobenzene with ICl - Iodobenzene (0.2 g; 0.1 mmole) and ICl (0.15 g; 0.1 mmole) were mixed together in a 10 ml Erlenmeyer flask which contained 5 ml of carbon tetrachloride. The stoppered flask was wrapped in foil and allowed to stand at room temperature. The initial reaction mixture which was a dark brown solution remained unchanged after three hours. Hydrogen chloride was not detected by iodometric analysis. Immeasurable traces of the isomeric chloriodobenzenes were detected by glpc analysis of the final reaction mixture.

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